

## Some Products from C=O Condensations of Quinacridones

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Quinacridone chemistry has been developed which provides a source of new compounds that have potential application in organic photovoltaic (OPV) devices. Phosphoryl chloride is used for the conversion of carbonyl groups in *N,N'*-dialkylquinacridones, generating reactive intermediates that enable selective condensation with either one or two nucleophilic molecules under mild conditions.

Manuscript received: 7 April 2020.

Manuscript accepted: 6 May 2020.

Published online: 25 August 2020.

## Introduction

With anthropogenic climate change potentially affecting all elements of the biosphere, efforts to mitigate the most significant of its effects by minimising carbon emissions are essential. Photovoltaic (PV) devices are a source of renewable energy that are critical to achieving this objective. Among the various PV device types that are being actively explored, solar cells based on organic materials demonstrate significant potential, due to their low production costs, high power-to-weight ratios, and the power conversion efficiencies (PCEs) of single junction devices now exceeding 18 %.

In particular, organic photovoltaics (OPVs) using soluble small molecules have attracted attention<sup>[1]</sup> due to their numerous favourable attributes, such as high purity, scalable synthesis, tuneable optoelectronic properties through molecular structural variation, and excellent stability.<sup>[2,3]</sup> As a result, a wide variety of planar small organic molecules have been evaluated for prospective utility in OPV devices. Both electron donor and electron acceptor molecules have been of interest, and while substantial progress has been made in the area of suitable donor molecules, promising acceptor molecules have been rather less abundant.

Fullerene-based compounds have long been among the most effective and popular single molecule electron acceptors since their first application. Gradual improvements have led to devices using this material giving PCEs in excess of 14 %.<sup>[4]</sup> Nevertheless, cost and other shortcomings have encouraged a continuing search for novel acceptor materials as alternatives for fullerenes. Several classes of well known commercial pigments, such as perylene diimides, phthalocyanines, and others, have shown some promise as n-type materials. The quinacridone (QA) nucleus (Fig. 1, Table 1, compounds **1a**, **1c**, **1f**), which has previously been extensively utilised in the preparation of light fast pigments, has also been investigated for photovoltaic utility, both in a role as an acceptor or donor molecule.<sup>[5]</sup>

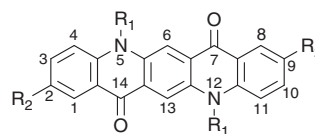


Fig. 1. Numbering scheme for substituted quinacridones.

Table 1. Common QAs and their *N*-octyl derivatives

Compound	R <sub>1</sub>	R <sub>2</sub>	Colour index name
<b>1a</b>	H	H	Pigment Violet 19
<b>1b</b>	octyl	H	
<b>1c</b>	H	Cl	Pigment Red 202
<b>1d</b>	octyl	Cl	
<b>1e</b>	H	Me	Pigment Red 122
<b>1f</b>	octyl	Me	

Substantial efforts have been devoted to the synthesis and characterisation of various QA derivatives, however, somewhat less attention has been paid to specifically modifying its optoelectronic properties. One route to modification is via condensation of the relatively unreactive carbonyl groups at C-7 and C-14 to afford molecules with extended conjugation and possibly other desirable electronic properties.<sup>[6]</sup> Some success has been achieved in condensing QAs with arylamines in the presence of titanium tetrachloride to form *N,N'*-dialkyl quinacridoneimines. Photophysical and electrochemical properties and temperature dependent geometrical isomerism in alkyl quinacridoneimines have been documented,<sup>[7]</sup> but these products had relatively low efficacy in solar cell trials when tested as p-type materials.

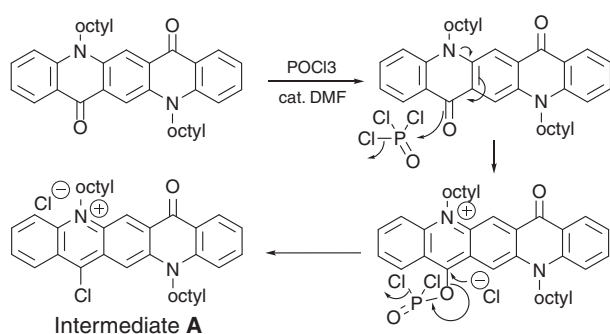
While Wang and others have been able to condense the carbonyl groups of *N,N'*-dialkylquinacridones with selected highly activated methylene groups in compounds such as malononitrile in a Knoevenagel-type condensation under prolonged reflux in acetic anhydride, the synthetic diversity available by this route has been limited.<sup>[8,9]</sup> Subsequent developments employing  $\text{TiCl}_4$ <sup>[10,11]</sup> to enable condensations have somewhat improved the accessibility of some condensed QAs, increasing the potential for producing candidate compounds for photovoltaic applications. Trials of a bis *N*-octylated dicyanoethylenated QA as an acceptor material in a solar cell with poly3-hexylthiophene (P3HT) as a donor gave encouraging conversion efficiencies up to 1.57 %.

While the power conversion efficiency achieved was relatively moderate, the study nevertheless confirmed the potential of a QA core, suitably condensed at the C=O groups, to provide a template worth exploring more extensively for designing improved acceptor molecules.<sup>[12]</sup> To this end, it was of interest to develop an alternative, more versatile, methodology for creating a wider variety of condensation products from diverse starting materials under mild conditions. In addition, if needed, several potentially useful QA variants bearing nuclear substituents such as 5,12-dichloro- (**1c**) and 5,12-dimethyl- (**1e**) are readily available commercially.

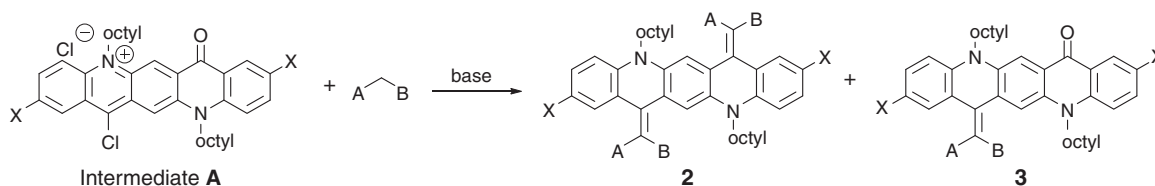
## Results and Discussion

During a search for reagents to effect activation of an *N*-alkylated QA with relatively unreactive carbonyl groups into a more active species, thereby rendering the molecule more amenable to condensations, an excess of  $\text{POCl}_3$  was added to an orange suspension of QA (**1a**) in 1,2-dichloroethane (DCE). When the mixture was stirred at 80°C for 1 h it darkened, and the suspended material dissolved to form an emerald green solution which did not change with further heating. When a portion of this reaction mixture was stirred with an excess of water it recovered its original orange colouration and TLC indicated only starting material was present.

The nature of the compound contained in the green solution was examined more closely. With deuteriochloroform as the



**Scheme 1.** Possible mechanism for the reaction of **1b** with  $\text{POCl}_3$  to give intermediate **A**.



**Scheme 2.** Reaction of intermediate **A** with activated  $-\text{CH}_2-$  groups to give bis- (**2**) and mono-condensed (**3**) derivatives of quinacridones.

reaction medium (containing a few drops of DMF as catalyst), a similar green solution was formed at room temperature over five days. The change from a symmetrical substitution pattern in the starting material (Fig. 1, Table 1, Fig. S1 (Supplementary Material), compound **1b**) to an unsymmetrical reaction product (Scheme 1, Fig. S2 (Supplementary Material), Intermediate **A**) was inferred from a doubling in the number of resonances observed in the  $^1\text{H}$  NMR spectrum. Particularly significant was the large downfield shift shown by one of the  $\text{N}-\text{CH}_2$  groups from  $\delta$  4.44 (in the starting QA **1b**) to  $\delta$  5.48, which was accompanied by a downfield shift of several of the 10 aromatic proton signals. This suggested a possible transformation to a quinacridinium salt (14-chloro-5,12-dimethyl-7-oxo-7,12-dihydroquinolino[2,3-*b*]acridin-5-ium chloride) (Intermediate **A**, Scheme 1). This inference is consistent with reactions observed subsequently with nucleophiles in the presence of an organic base. The absence of any indication of  $\text{P}-\text{O}-\text{C}(14)$  coupling in the  $^{13}\text{C}$  NMR spectrum suggests that while a phosphate may have formed initially, it was readily converted into a reactive 14-chloro species in a manner resembling a vinylogous Vilsmeier reaction (Scheme 1).

From a consideration of the  $^1\text{H}$  NMR spectrum of intermediate **A**, it seems likely that phosphoryl chloride ( $\text{POCl}_3$ ) initially forms a mono quaternary salt which, as a consequence, now renders the molecule significantly more electron deficient and inhibits a similar conversion of the second carbonyl group. When the positive charge is discharged by condensation with a suitable nucleophile the ability to generate a reactive quaternary species is restored. This leads to a second activation step, and the second  $\text{C}=\text{O}$  is converted into a species amenable to further condensation and the formation of a bis-condensed product. Thus, even with a large excess of  $\text{POCl}_3$  present it was feasible, by limiting the reaction time, to synthesise a mainly mono-condensed product which could be isolated, the second carbonyl group activated, and condensation effected with a different nucleophile.

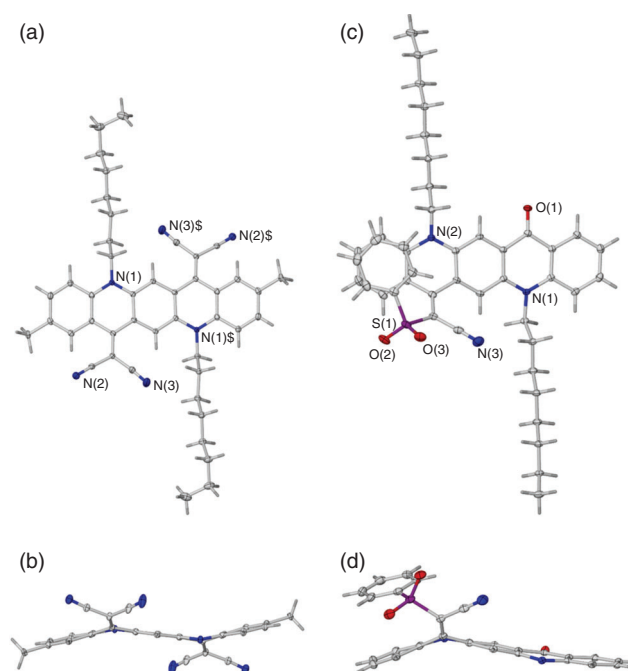
### Condensations with Activated $-\text{CH}_2-$ Groups

When a reaction was carried out with the green solution described above with an excess of methyl cyanoacetate at room temperature overnight in the presence of 2,4,6-collidine the bis product **2a** was formed in 74 % yield. Several similar products (Scheme 2, Table 2) were obtained under comparable conditions with a variety of compounds, with the principal requirement for condensation being a methylene group sufficiently activated by flanking electron-withdrawing groups. An example of the conformation adopted by a representative of these bis-condensed products, **2b**, in the solid state as determined by X-ray crystallography is shown in Fig. 2a, b. A monocondensed product **3d** is shown in Fig 2c, d.

Alternatively, in order to favour mono-condensation, the green solution was cooled to 0°C and treated with an excess of methyl cyanoacetate followed by triethylamine. After 2 h at room temperature the mixture was quenched with ethyl acetate

**Table 2.** Bis- and monocondensed QA derivatives formed by the reaction of Intermediate A with an activated  $-\text{CH}_2$  group

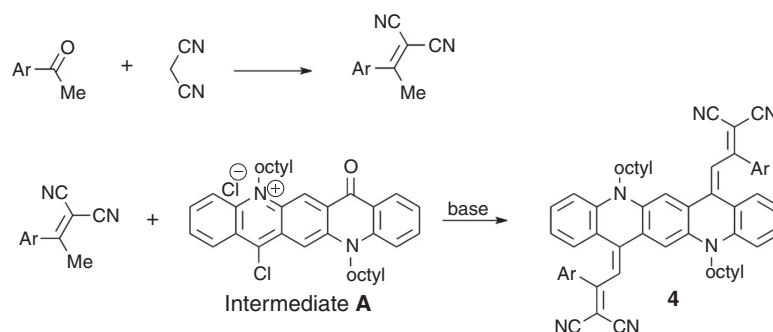
Compound	A—B	X	Yield [%]	Compound	A—B	X	Yield [%]
<b>2a</b>		H	74	<b>3a</b>		H	74
<b>2b</b>		Me	66	<b>3b</b>		H	85
<b>2c</b>		Cl	58	<b>3c</b>		Me	52
<b>2d</b>		H	66	<b>3d</b>		H	74
				<b>3e</b>		H	79

**Fig. 2.** (a) Molecular unit in the crystal structure of **2b**. Ellipsoids shown at 50 % probability. Symmetry element used:  $\$ = -x, -y, -z$ . (b) Side view of quinacridone core, showing armchair conformation. Octyl groups omitted for clarity. (c) Molecular unit in the crystal structure of **3d**. Ellipsoids shown at 50 % probability. (d) Side view of quinacridone core, showing armchair conformation. Octyl groups omitted for clarity.

and water. Chromatography (silica gel/DCM) of the material contained in the organic phase yielded a blue mono adduct (**3a**, 74 %). Similarly, a brief reaction with an excess of malononitrile also gave a mono-condensed product (**3b**, 85 %). Several organic bases, such as triethylamine, diisopropylethylamine, and 2,4,6-collidine, were effective in promoting these condensations, with 2,4,6-collidine being the most effective. In all cases the presence of a substantial excess of both  $\text{POCl}_3$  and the nucleophilic component was tolerated and formation of the bis-condensation product could be enhanced by extending the reaction time or by gently warming the reaction mixture. Whether the routine addition of an excess of the nucleophilic component had any significant effect on the yield or rate of formation of the products was not investigated.

Surprisingly, it was subsequently found that it was unnecessary to preprepare a solution of the green reactive intermediate before reaction with a nucleophile, and indeed

the condensations proceeded quite readily when a mixture containing the QA, an excess of  $\text{POCl}_3$ , the nucleophilic component, and an organic base was stirred at room temperature. In all reactions, progress was conveniently monitored by examining the TLC plate of a quenched aliquot, which showed the initial emergence of a major blue or violet component accompanied by a minor green spot that represented the bis-adduct, which gradually increased in relative intensity at the expense of the mono product. In general, the condensations were surprisingly tolerant of the number of reaction equivalents of the reacting compounds. Thus, with one equivalent of QA or mono-condensed QA, satisfactory condensation products were isolated from reaction mixtures containing from 3 to 5 equivalents of  $\text{POCl}_3$  and  $>1$  equivalent of the nucleophilic coupling component. Progress of the condensation was readily monitored by quenching a small sample from the reaction solution and observing the elution of distinctive coloured spots, which were



**Scheme 3.** Condensation of intermediate **A** with  $\text{ArC}(\text{CH}_3)=\text{C}(\text{CN})_2$ .

**Table 3.** Condensation products from  $\text{ArC}(\text{CH}_3)=\text{C}(\text{CN})_2$

Compound	Ar	Yield [%]
4a		62
4b		55
4c		36

easily identifiable as starting material, mono-condensed, and biscondensed entities. As expected, prolonged reaction favoured formation of bis-products, especially in the presence of 2,4,6-collidine as a base (Table 2).

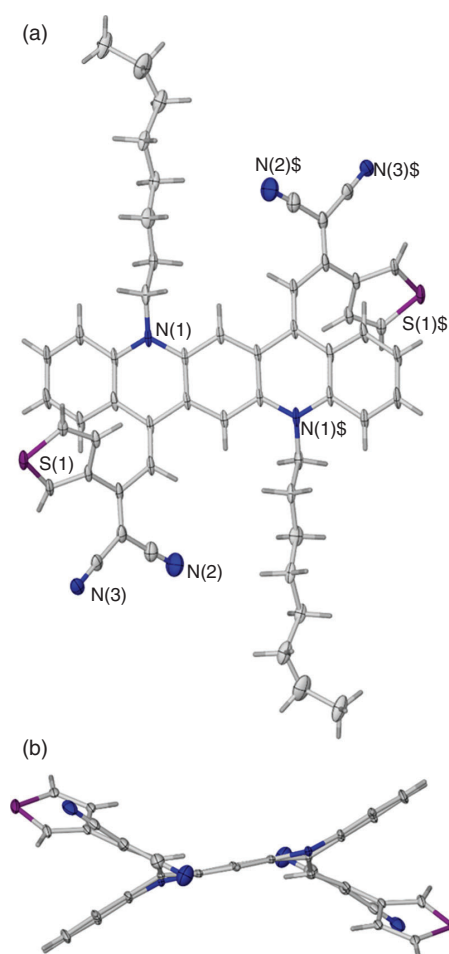
#### Condensations with Activated $-\text{CH}_3$ Groups

Condensation of the reactive green QA intermediate could also be affected with activated methyl groups. Substrates sufficiently activated for such reactions were obtained by condensing acetophenones with malononitrile<sup>[13]</sup> to generate a product of the type  $\text{ArC}(\text{CH}_3)=\text{C}(\text{CN})_2$ , in which the  $\text{CH}_3$  group was sufficiently reactive for condensation to occur (Scheme 3). Several compounds bearing this moiety were successfully condensed (Scheme 3, Table 3). This procedure may be of some potential value to produce products with enhanced pi conjugation due to the greater planarity that could result from relatively less congestion at the newly formed methylene group. An example of the conformation of a representative of this group **4c** as determined by X-ray crystallography is shown in Fig. 3.

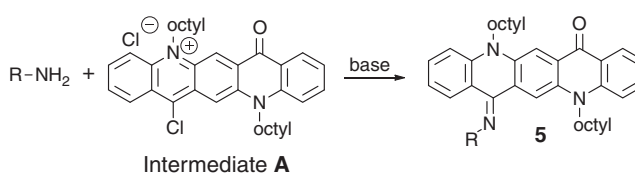
#### Condensations with $\text{R}-\text{NH}_2$ Groups

In addition, it was also found that primary amino groups reacted readily (Scheme 4, Fig. 4). This synthesis was readily extended to affect successful condensations with amides ( $-\text{CONH}_2$ ), 1,1-disubstituted ureas ( $\text{R}_1\text{R}_2\text{NCONH}_2$ ), as well as an aryl sulfonamide ( $\text{ArSO}_2\text{NH}_2$ ) (Table 4).

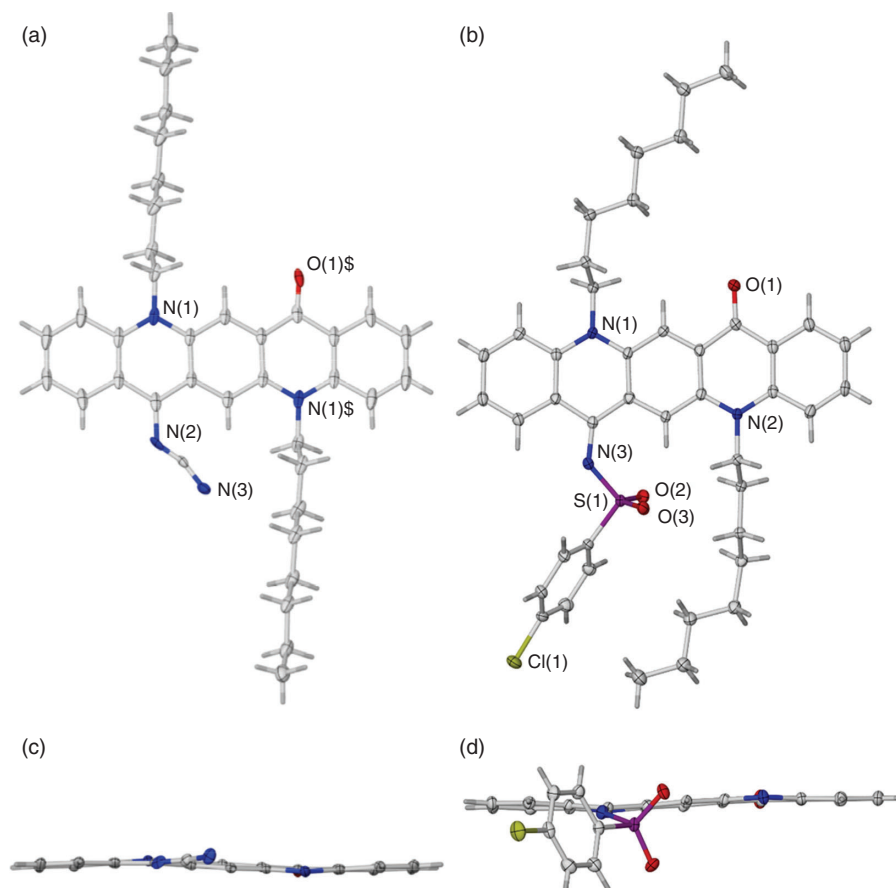
Owing to their industrial applications as versatile pigments, several ring substituted QAs are commercially available. With the intention of evaluating the effect that a change in nuclear substitution might have on the photovoltaic properties of derivatives of the type previously described, a sample of Pigment Red 202 (**1c**, Colour Index 73907) was purchased and duly alkylated as received with *n*-octyl



**Fig. 3.** (a) Molecular unit in the crystal structure of **4c**. Symmetry operator:  $\$ = 1 - x, -y, 1 - z$ . Hydrogen atoms and one disordered position of octyl group omitted for clarity. (b) Side view of quinacridone core, showing armchair conformation. Octyl groups and hydrogen atoms omitted for clarity.



**Scheme 4.** Reaction of intermediate **A** with  $\text{R}-\text{NH}_2$ .



**Fig. 4.** (a) Molecular unit in the crystal structure of **5a**. Ellipsoids shown at 30 % probability. Symmetry element used:  $1-x, 1-y, -z$ . (b) Molecular unit in the crystal structure of **5b**. Ellipsoids shown at 50 % probability. Symmetry element used:  $\$ = 1-x, 1-y, -z$ . (c) Side view of quinacridone core of **5a**, showing near planar conformation. Octyl groups omitted for clarity. (d) Side view of quinacridone core of **5b**, showing near planar conformation of the quinacridone core. Octyl groups omitted for clarity.

**Table 4.** Quinacridone derivatives formed by the mono-condensation of amines

Compound	R-NH <sub>2</sub>	Yield [%]
<b>5a</b>		73
<b>5b</b>		72
<b>5c</b>		68

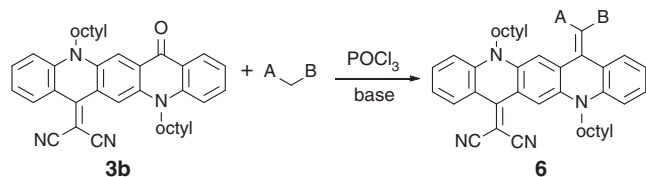
bromide. Pigment Red 202 is usually assumed to be the 2,9-dichloro derivative of QA. Rather surprisingly, the product from alkylation of this commercial sample was found to consist of two dioctylated species which were formed in comparable quantities and consisted of a mixture of 5,12-dioctyl-2,9-dichloroquinacridone (**1d**) and 5,12-dioctyl-2,9-dimethylquinacridone (**1f**). Evidently the QA sample as supplied was not a single entity as expected but in fact consisted of a blend of Pigment Red 202 (**1c**) and Pigment Red 122 (**1e**) in similar proportions. After separation, each of these analogues, in the presence of POCl<sub>3</sub>, readily gave products analogous to those observed with the unsubstituted parent (**Table 5**). Although the mixture as supplied

**Table 5.** Asymmetric QA derivatives formed by the condensation of a nucleophile with mono-condensed quinacridone **3b** (**Scheme 5**)

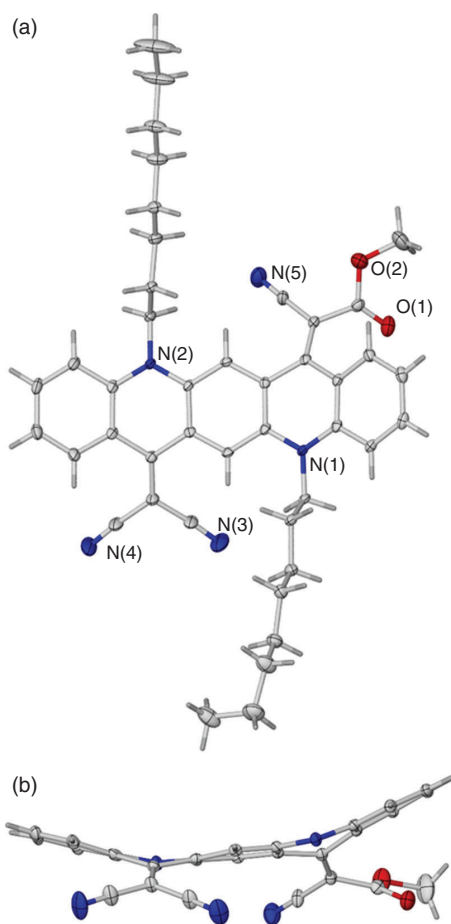
Compound	A-B	Yield [%]
<b>6a</b>		62
<b>6b</b>		63
<b>6c</b>		70
<b>6d</b>		66
<b>6e</b>		84

(after *N*-alkylation) readily condensed with nucleophiles in the presence of POCl<sub>3</sub> to give the expected products as a mixture, it was more convenient to simplify subsequent purifications by





**Scheme 5.** Reaction of mono-condensed quinacridone **3b** with a nucleophile to yield an asymmetric bis-condensed quinacridone derivative.



**Fig. 5.** (a) Molecular unit in the crystal structure of **6a**. Ellipsoids shown at 50% probability, one position of the disordered methyl group of an octyl group removed for clarity. (b) Side view of quinacridone core, showing armchair conformation. Octyl groups omitted for clarity.

carrying out the condensations with the previously separated individual QAs.

#### Condensation with a Different Second Component

Mono-condensed products, such as the initial product **3b** obtained from malononitrile, were readily prepared and isolated from reactions employing short reaction times. Hence it became possible to activate the remaining C=O as a separate second step initiated by a second charge of POCl<sub>3</sub>. This enabled a stepwise introduction of a second substituent to yield a molecule with asymmetric electron flow characteristics, potentially enabling graduated tuning of various electronic properties. Notably, in an example of a product of this reaction that was characterised by X-ray crystallography, **6a**, the QA moiety adopted a concave morphology (Fig. 5), which was

in direct contrast to the planar or armchair morphologies observed for the products of the condensations with R-NH<sub>2</sub> groups (Fig. 4) and the bis-condensation with malononitrile (Fig. 3), respectively.

#### UV-Visible Spectra

The spectra of representative compounds of structural type **2–6** were determined (Fig. 6). Significantly, each of each of these groups showed intense absorption in the range 650 to 750 nm, an energy rich range of the visible spectrum over which the popular n-type fullerene acceptors have low absorption. The newly synthesised QAs of structural type **4** showed particularly strong absorption in this region.

#### Conclusions

A new method has been developed which enables dialkylated QAs to be transformed under mild conditions to reactive intermediates which readily condense with a variety of nucleophilic components to yield condensed products. The reaction conditions can be modified to select either bis-condensed products utilising both carbonyl groups at once or mono-condensed products in which the second carbonyl group can be activated and condensed with a second, different, nucleophile. This work provides a pathway to a variety of highly substituted quinacridone derivatives, allowing for customisation of their optoelectronic and physical properties, which is potentially useful in the fabrication of bulk hetero-junction solar cells.

#### Experimental

##### Methods and Materials

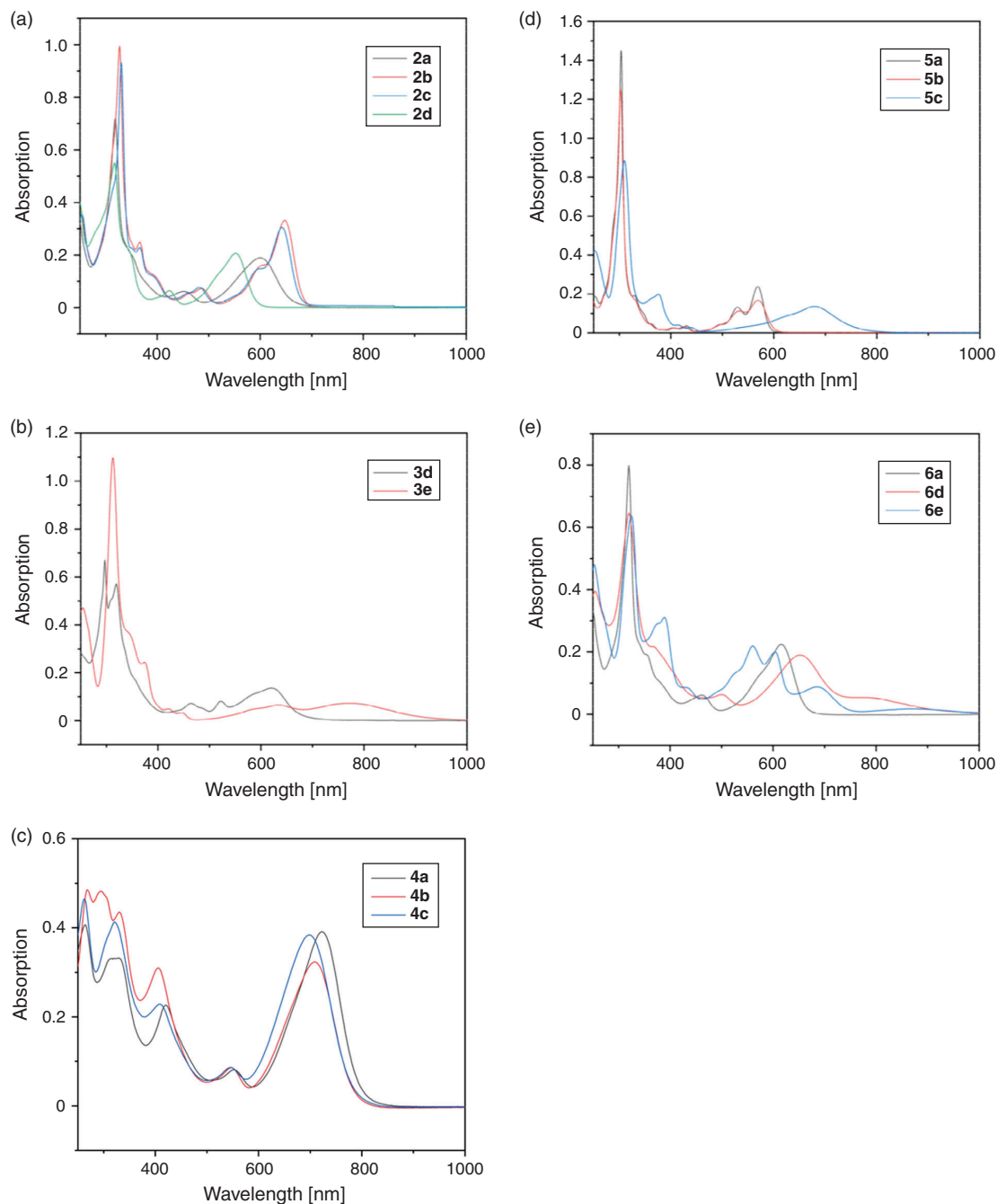
QA was purchased from Tokyo Kasei Kogyo Co. and a QA described as CI 202 was purchased from Winchem Industrial Co Ltd, China. Both compounds were used without further purification. *N*-(*n*-Octyl)-*N'*-(*n*-octyl)quinacridone was prepared by the literature method<sup>[14]</sup> with minor modifications.

Analytical TLC was performed on Merck Kiesegel 60 F<sub>254</sub> silica aluminium backed sheets, and was visualised under visible or UV light. Column chromatography was performed on Merck Kiesegel (particle size: 0.04–0.063 mm) silica gel.

NMR spectra were recorded with a Bruker UltraShield Avance III 400 MHz Spectrometer running the *TopSpin 2.1* software package at 293 K. CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as solvents and as an internal lock. Chemical shifts are measured in ppm. <sup>1</sup>H NMR chemical shifts were referenced to δ 7.26 for CDCl<sub>3</sub> and δ 2.50 for DMSO-*d*<sub>6</sub>. Spectra were run routinely as a solution in deuteriochloroform unless otherwise stated. <sup>13</sup>C NMR were run in CDCl<sub>3</sub> at 100.6 MHz unless otherwise stated; chemical shifts were referenced to δ 77.0 for CDCl<sub>3</sub> and δ 39.52 for DMSO-*d*<sub>6</sub>. Spectroscopic data were reported using the following format: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), *J*-coupling constant (Hz), assignment. Dichloromethane is abbreviated as DCM and 1,2-dichloroethane as DCE.

Melting points were determined using a Gallenkamp hot-stage microscope and are uncorrected.

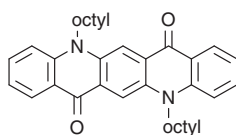
Atmospheric pressure chemical ionisation (APCI)/atmospheric sample analysis probe (ASAP) mass spectrometry, including high resolution experiments, were carried out on a Thermo Scientific Q Exactive FTMS employing ASAP/APCI probes.



**Fig. 6.** UV-Visible spectra of compounds (a) **2a–d**, (b) **3d–e**, (c) **4a–c**, (d) **5a–c**, and (e) **6a, d–e**.

### Synthesis

#### 5,12-Di(*n*-octyl)quinacridone (**1b**) (Chart 1)



**Chart 1.**

*n*-Octyl bromide (19.3 g, 100 mmol) was added to a suspension of QA (10.41 g, 30 mmol) in a mixture of hexamethylphosphoramide (80 mL) and benzene (120 mL) followed by

addition of sodium hydride (4.5 g, 60 % in oil) over 6 h. The blue mixture was stirred for 7 d at room temperature and the excess of hydride was destroyed with 50 % aq. *i*PrOH (5 mL). The benzene was evaporated and the mixture was diluted with a mixture of methanol (150 mL) and water (5 mL). The precipitate was filtered off the next day and purified by chromatography over alumina. Elution with dichloromethane containing ethyl acetate (up to 10 %) gave the product (14.7 g, 64 %) as orange needles, sufficiently pure for subsequent reactions.  $\delta_{\text{H}}$  8.66 (2H, s,  $2 \times \text{ArH}$ ), 8.50 (2H, m,  $2 \times \text{ArH}$ ), 7.7 (2H, m,  $2 \times \text{ArH}$ ), 7.43 (2H, d,  $J$  8.8,  $2 \times \text{ArH}$ ), 4.44 (4H, m,  $2 \times \text{CH}_2\text{N}$ ), 1.95 (4H, m,  $2 \times \text{CH}_2$ ), 1.60 (4H, m,  $2 \times \text{CH}_2$ ), 1.45 (4H, m,  $2 \times \text{CH}_2$ ), 1.30 (12H, m,  $6 \times \text{CH}_2$ ), 0.88 (6H, m,  $2 \times \text{CH}_3$ ).

14-Chloro-5,12-dioctyl-7-oxo-7,12-dihydroquinolino[2,3-b]acridin-5-ium chloride (Intermediate A) (Chart 2)

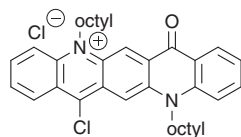


Chart 2.

$\delta_{\text{H}}$  ( $\text{CDCl}_3 + \text{DMF}$ ) 9.53 (1H, s, ArH), 8.82 (1H, m, ArH), 8.73 (1H, s, ArH), 8.58 (1H, m, ArH), 8.58 (1H, m, ArH), 8.44 (1H, m, ArH), 8.0 (1H, m, ArH), 7.89 (1H, m, ArH), 7.59 (1H, d,  $J$  8.8, ArH), 7.36 (1H, m, ArH), 5.48 (2H, m,  $-\text{NCH}_2-$ ), 4.54 (2H, m,  $-\text{NCH}_2-$ ), 2.23 (2H, m,  $\text{CH}_2$ ), 2.08 (2H, m,  $\text{CH}_2$ ), 1.2–1.8 (20H, m,  $10 \times \text{CH}_2$ ), 0.87 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  ( $\text{CDCl}_3 + \text{DMF}$ ) 177.2, 153.8, 142.5, 141.0, 140.3, 140.0, 136.7, 133.8, 130.3, 129.7, 128.5, 127.9, 127.2, 126.0, 122.8, 121.1, 118.7, 118.6, 115.2, 110.8, 52.1, 47.1, 31.7, 31.6, 29.6, 29.3, 29.2, 29.1, 29.0, 26.9, 26.2, 22.6, 22.5, 14.1, 14.0.

2,9-Dichloro-5,12-dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-dione (**1d**) and 2,9-Dimethyl-5,12-dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-dione (**1f**) (Chart 3)

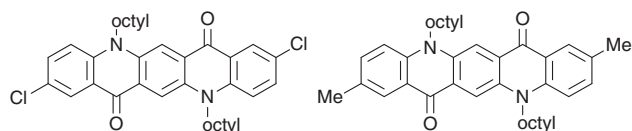


Chart 3.

The mixture of QAs supplied as Colour Index Pigment Red 202 (18 g) and *n*-octyl bromide (30 g, 155 mmol) in a mixture of hexamethylphosphoramide (300 mL) and benzene (600 mL) was boiled down to a volume of ~360 mL and tetrabutylammonium bromide (2 g) was added. The mixture was cooled and a portion of sodium hydride (2 g of 8.4 g, 60% in oil) added. After stirring for 5 h at 40°C and then for 2 d at room temperature more sodium hydride (1 g) was added at 50°C, the rest of the hydride was then added over 4 h. After 48 h the mixture was cooled to room temperature and quenched by the slow addition of aqueous methanol (90%, 100 mL). Filtration and washing of the precipitate with methanol gave a mixture of the crude products as red needles (28.7 g). A portion (1 g) of the above material was chromatographed over silica gel and 2,9-dichloro-5,12-dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-dione (**1d**, 0.32 g), mp 260–262°C, was eluted with DCM/5% ethyl acetate.  $\delta_{\text{H}}$  8.48 (2H, s,  $2 \times \text{ArH}$ ), 8.28 (2H, s,  $2 \times \text{ArH}$ ), 7.57 (2H, dd,  $J$  8.8, 2.0,  $2 \times \text{ArH}$ ), 7.30 (2H, d,  $J$  9.3,  $2 \times \text{ArH}$ ), 4.37 (4H, m,  $2 \times \text{CH}_2\text{N}$ ), 1.88 (4H, m,  $2 \times \text{CH}_2$ ), 1.59 (8H, m,  $4 \times \text{CH}_2$ ), 1.2–1.6 (16H, m,  $8 \times \text{CH}_2$ ), 1.88 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  (125.7 MHz) 176.3, 140.1, 135.0, 134.5, 126.7(2C), 125.4, 121.1, 116.6, 113.4, 46.7, 32.0, 29.6, 29.5, 27.2(2C), 22.85, 14.3.  $m/z$  604.2618; calcd for  $\text{C}_{36}\text{H}_{42}\text{Cl}_2\text{N}_2\text{O}_2$  604.2623.

This was followed by the 2,9-dimethyl product (**1f**, 0.44 g) which was recrystallised from acetic acid to give red needles, mp 234–236°C.  $\delta_{\text{H}}$  8.62 (2H, s,  $2 \times \text{ArH}$ ), 8.24 (2H, br s,  $2 \times \text{ArH}$ ), 7.48 (2H, dd,  $J$  8.8, 2.0,  $2 \times \text{ArH}$ ), 7.55 (2H, dd,  $J$  8.8, 2.0,  $2 \times \text{ArH}$ ), 4.45 (4H, t,  $J$  8.0,  $2 \times \text{CH}_2\text{N}$ ), 2.42 (6H, s,  $2 \times \text{ArCH}_3$ ), 1.90 (4H, m,  $2 \times \text{CH}_2$ ), 1.60 (4H, m,

$2 \times \text{CH}_2$ ), 1.45 (4H, m,  $2 \times \text{CH}_2$ ), 1.35 (12H, m,  $6 \times \text{CH}_2$ ), 0.86 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  179.4, 141.9, 137.5, 136.9, 131.8, 128.7, 127.5, 122.3, 116.1, 114.8, 47.8, 33.35, 31.0, 30.9, 29.7, 28.6, 24.2, 22.1, 15.65.  $m/z$  564.3710; calcd for  $\text{C}_{38}\text{H}_{48}\text{N}_2\text{O}_2$  564.3716.

### General QA Condensation Methods

#### Method A (for Bis-condensed Products)

5,12-Dioctylquinacridone (**1b**) (0.54 g, 1 mmol) was suspended in DCE (15 mL) containing DMF (2 drops) and  $\text{POCl}_3$  (3 mmol), and the mixture was stirred at 60°C for 2 h. The substrate (4 mmol) and 2,4,6-collidine (8 mmol) were added to the clear green solution at room temperature and the reaction was continued for 48 h. The mixture was added to aqueous citric acid (15%, 100 mL), stirred for 20 min, and extracted with ethyl acetate ( $2 \times 50$  mL). The organic phase was separated, the volatile components removed by evaporation, and the residue was chromatographed over silica gel.

#### Method B (for Mono-condensed Products)

The green reactive intermediate was prepared from the quinacridone (1 mmol) as in Method A above. The substrate (2 mmol) and 2,4,6-collidine (8 mmol) were added to the clear green solution at room temperature and the reaction was continued for 2 h. The mixture was worked up as in Method A.

#### Method C (Malononitrile Mono-condensation Product **3b** Coupling with a Second Component)

A mixture of the malononitrile monocondensation product (**3b**, 0.58 g, 1 mmol), DCE (15 mL), DMF (2 drops), and  $\text{POCl}_3$  (0.45 g, 3 mmol) was stirred at 60°C for 2 h and then cooled to room temperature. The nucleophilic component (2 mmol) was added followed by triethylamine (6 mmol) and the mixture was stirred for 24 h at room temperature. The mixture was worked up as in Method A.

#### Method D (All Components Combined at the Start of Reaction)

A stirred mixture of the 5,12-dioctylquinacridone (1 mmol), DCM (20 mL), and  $\text{POCl}_3$  (0.6 g, 4 mmol) at 0°C was treated with the nucleophilic component (4 mmol) added in one portion followed by diisopropylethylamine or 2,4,6-collidine (10 mmol), and allowed to react overnight at room temperature. The next day the mixture was worked up as in Method A.

#### Adducts Using an Activated $-\text{CH}_2-$

#### Dimethyl 2,2'-(5,12-dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-diylidene)bis(2-cyanoacetate) (**2a**) (Chart 4)

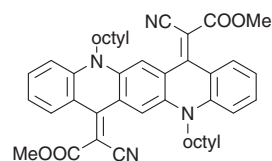


Chart 4.

Method A: Methyl cyanoacetate (0.40 g, 4 mmol) was reacted with 5,12-dioctylquinacridone (0.54 g, 1 mmol). The material which was eluted from silica gel with light petroleum/DCM



(1 : 4) was collected and crystallised from DCM/methanol to afford **2a** as long blue needles (0.52 g, 74 % based on 1 mmol 5,12-dioctylquinacridone), mp 171–173°C.  $\delta_{\text{H}}$  8.49 (2H, br s, 2  $\times$  ArH), 7.78 (2H, m, 2  $\times$  ArH) 7.60 (2H, m, 2  $\times$  ArH), 7.38 (2H, m, 2  $\times$  ArH), 7.14 (2H, m, 2  $\times$  ArH), 4.33 (4H, m, 2  $\times$  CH<sub>2</sub>N), 3.81 (6H, s, 2  $\times$  OCH<sub>3</sub>), 2.0 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.24–1.67 (20H, m, 10CH<sub>2</sub>), 0.90 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  166.9, 153.65, 141.2, 135.2, 134.4, 130.6, 125.0, 122.1, 121.4, 119.65, 115.5, 112.7, 93.6, 54.3, 50.1, 33.3, 30.84, 30.82, 28.44, 28.31, 24.2, 15.7.  $m/z$  698.3827; calcd for C<sub>44</sub>H<sub>50</sub>N<sub>4</sub>O<sub>4</sub> 698.3832.

2,2'-(2,9-Dimethyl-5,12-dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-diylidene)dimalononitrile (**2b**) (Chart 5)

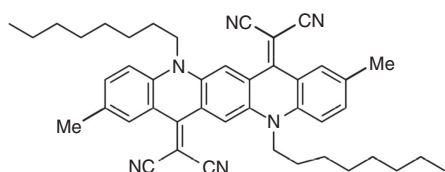


Chart 5.

Method A: 2,9-Dimethyl-5,12-dioctylquinacridone (**1d**) (0.56 g, 1 mmol) was reacted with malononitrile (0.25 g, 4 mmol). The residue was chromatographed over silica and the product was eluted with DCM/light petroleum (3 : 1) and crystallised from ethyl acetate to give dark green needles of **2b** (0.43 g, 66 % based on 1 mmol of 2,9-dimethylquinacridone), mp 200–202°C.

Method D: 2,9-Dimethyl-5,12-dioctylquinacridone (**1d**) (0.56 g, 1 mmol) was reacted with malononitrile (0.25 g, 4 mmol) and POCl<sub>3</sub> (0.52 g, 4 mmol) to give 0.37 g (56 %) of **2b**.

$\delta_{\text{H}}$  (500 Mz) 8.7 (2H, s, 2  $\times$  ArH), 8.35 (2H, s, 2  $\times$  ArH), 7.60 (2H, m, 2  $\times$  ArH), 7.40 (2H, m, 2  $\times$  ArH), 4.45 (4H, t,  $J$  7.8, 2  $\times$  CH<sub>2</sub>N), 2.46 (6H, s, 2  $\times$  ArCH<sub>3</sub>), 1.98 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.40–1.60 (20H, m, 10  $\times$  CH<sub>2</sub>), 0.85 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  154.3, 137.0, 135.0, 133.0, 131.4, 126.2, 122.3, 117.4, 116.7, 116.7, 114.0, 111.1, 69.4, 48.7, 31.4, 28.9, 26.7, 26.4, 22.29, 20.4, 13.7.  $m/z$  660.3935; Calcd for C<sub>44</sub>H<sub>48</sub>N<sub>6</sub> 660.3940.

2,2'-(2,9-Dichloro-5,12-dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-diylidene)dimalononitrile (**2c**) (Chart 6)

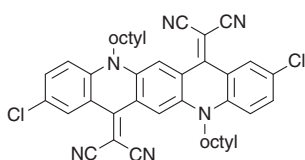


Chart 6.

Method A: 2,9-Dichloroquinacridone (0.64 g, 1 mmol) and malononitrile (0.25 g, 4 mmol) were treated as above and the crude product was applied to a silica column and eluted with 1 : 1 DCM/light petroleum and crystallised from DCM/ethanol to give the product **2c** (0.41 g, 58 % based on the QA) as green granules, mp 220–222°C.  $\delta_{\text{H}}$  8.58 (2H, s, 2  $\times$  ArH), 8.52 (2H, m, 2  $\times$  ArH), 7.69 (2H, dd,  $J$  9.2, 2.3, 2  $\times$  ArH), 7.47 (2H, m,

2  $\times$  ArH), 4.45 (4H, m, 2  $\times$  CH<sub>2</sub>N), 2.0 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.50 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.25–1.48 (12H, m, 6  $\times$  CH<sub>2</sub>), 1.35 (6H, t,  $J$  8.1, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  155.13, 139.34, 135.94, 135.21, 129.04, 127.74, 124.29, 119.39, 118.61, 117.70, 117.61, 113.36, 72.91, 50.96, 33.30, 30.79, 30.77, 28.56, 28.32, 24.22, 15.69.  $m/z$  700.2843; calcd for C<sub>42</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>6</sub> 700.2848.

2,2'-(5,12-Dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-diylidene)bis(3-oxo-3-(pyrrolidin-1-yl)propanenitrile) (**2d**) (Chart 7)

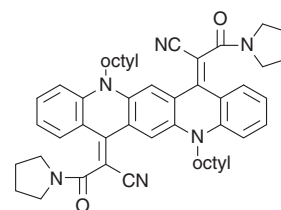


Chart 7.

Method A: Compound **2d** was prepared from 3-oxo-3-(pyrrolidin-1-yl)propanenitrile (0.52 g, 4 mmol) and the QA (**1b**, 1 mmol) followed by work up and chromatography over silica gel and eluted with 1 : 1 DCM/light petroleum and crystallised from DCM/ethanol to give blue needles (0.50 g, 66 % based on the QA), mp 183–185°C.  $\delta_{\text{H}}$  8.19 (2H, s, 2  $\times$  ArH), 8.36 (2H, m, 2  $\times$  ArH), 7.47 (2H, m, 2  $\times$  ArH), 7.25 (2H, m, 2  $\times$  ArH), 7.03 (2H, m, 2  $\times$  ArH), 4.24 (4H, m, 2  $\times$  CH<sub>2</sub>N), 3.50 (4H, m, 2  $\times$  CH<sub>2</sub>NCH<sub>2</sub>), 2.87 (4H, br m, 2  $\times$  CH<sub>2</sub>NCH<sub>2</sub>), 1.2–1.95 (32H, m 16  $\times$  CH<sub>2</sub>), 0.85 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  162.8, 144.8, 138.9, 133.8, 131.4, 126.7, 122.45, 120.3, 118.85, 117.7, 113.25, 110.67, 98.44, 37.45, 46.44, 45.68, 31.41, 29.0, 28.9, 26.6, 26.0, 25.0, 24.0, 22.3, 13.7.  $m/z$  776.4772; calcd for C<sub>50</sub>H<sub>60</sub>N<sub>6</sub>O<sub>2</sub> 776.4778.

Methyl 2-Cyano-2-(5,12-dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)acetate (**3a**) (Chart 8)

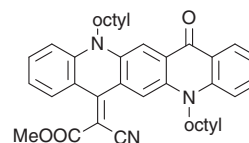


Chart 8.

Method B: Methyl cyanoacetate (0.20 g, 2 mmol) was reacted with **1b** (0.54 g, 1 mmol). After work up the material contained in the organic phase was purified (SiO<sub>2</sub>/DCM) and crystallised from methanol to afford **3a** (0.46 g, 74 %) as purple, woolly needles, mp 151–153°C.  $\delta_{\text{H}}$  8.50 (3H, m, 3  $\times$  ArH), 7.03–7.83 (7H, m, 7  $\times$  ArH), 4.37 (2H, m, CH<sub>2</sub>N), 4.28 (2H, m, CH<sub>2</sub>N), 3.28 (3H, s, OCH<sub>3</sub>), 1.93 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.2–1.6 (24H, m, 12  $\times$  CH<sub>2</sub>), 0.66 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  178.8, 166.6, 153.8, 143.6, 141.4, 137.4, 136.2, 135.2, 134.4, 130.3, 129.5, 122.7, 122.6, 122.0, 121.0, 119.5, 116.2, 115.5, 115.4, 114.5, 112.9, 54.35, 54.3, 49.3, 48.6, 33.4, 33.3, 30.9, 30.88, 30.86, 30.83, 28.85, 28.6, 28.5, 28.0, 24.2, 15.68, 15.66.  $m/z$  617.3613; calcd for C<sub>40</sub>H<sub>47</sub>N<sub>3</sub>O<sub>3</sub> 617.3617.

2-(5,12-Dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)malononitrile (**3b**) (Chart 9)

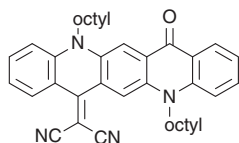


Chart 9.

Method B: Malononitrile (0.13 g, 2 mmol) was reacted with QA **1b** (0.54 g, 1 mmol). After work up the residue was crystallised from methanol (15 mL) to give **3b** (0.50 g, 85.3 % based on **1b**), mp 155–157°C.  $\delta_{\text{H}}$  8.67 (2H, s, 2  $\times$  ArH), 8.54 (2H, m, 2  $\times$  ArH), 7.73 (2H, m, ArH), 7.51 (1H, d,  $J$  8.8, ArH), 7.47 (1H, d,  $J$  8.4 Hz, ArH), 7.30 (2H, m, 2  $\times$  ArH), 4.45 (4H, m, 2  $\times$  CH<sub>2</sub>N), 2.04 (4H, m, 2  $\times$  CH<sub>2</sub>) 1.25–1.68 (20H, m, 10  $\times$  CH<sub>2</sub>), 0.89 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  177.4, 155.8, 142.3, 139.4, 136.1, 135.0, 134.2, 133.1, 128.1, 127.3, 125.6, 123.1, 121.5, 121.4, 121.3, 117.7, 117.0, 116.9, 114.8, 114.25, 112.5, 112.4, 70.25, 48.1, 47.3, 31.83, 31.76, 29.5, 29.30, 29.28, 27.2, 27.0, 26.9, 26.7, 22.7, 22.65, 14.14, 14.11.  $m/z$  584.3510; calcd for C<sub>39</sub>H<sub>44</sub>N<sub>4</sub>O 584.3515.

2-(2,9-Dimethyl-5,12-dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)malononitrile (**3c**) (Chart 10)

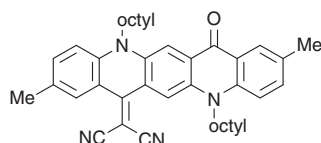


Chart 10.

Method B: 2,9-Dimethylquinacridone (**1f**) (0.56 g, 1 mmol) was reacted with malononitrile (0.12 g, 2 mmol). The residue was chromatographed over silica and **3c** was eluted with DCM/light petroleum (5 : 1) and crystallised as stout needles (0.32 g, 52 % based on **1f**) from DCM/ethanol, mp 154–156°C.  $\delta_{\text{H}}$  8.64 (2H, s, 2  $\times$  ArH), 8.30 (2H, m, 2  $\times$  ArH), 7.59 (2H, m, 2  $\times$  ArH), 7.41 (2H, m, 2  $\times$  ArH), 4.46 (4H, m, 2  $\times$  CH<sub>2</sub>N), 2.46, 2.46 (3H, 3H, s, s, 2  $\times$  ArCH<sub>3</sub>), 1.98 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.3–1.7 (20H, m, 10  $\times$  CH<sub>2</sub>), 1.38 (6H, m, 2  $\times$  CH<sub>3</sub>), 0.9 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  (125.7 MHz) 178.6, 156.8, 142.0, 138.1, 137.3, 134.4, 132.8, 132.6, 128.7, 128.2, 126.7, 124.5, 122.4, 119.5, 118.9, 118.4, 116.4, 115.8, 114.0, 113.7, 70.6, 49.5, 48.7, 33.4, 33.3, 30.9, 30.8 (2  $\times$  C), 28.8, 28.6, 28.5, 28.3, 22.9, 22.8, 20.9, 20.75, 14.3, 14.2.  $m/z$  612.3823; calcd for C<sub>41</sub>H<sub>48</sub>N<sub>4</sub>O 612.3828.

2-(5,12-Dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)-2-(phenylsulfonyl)acetonitrile (**3d**) (Chart 11)

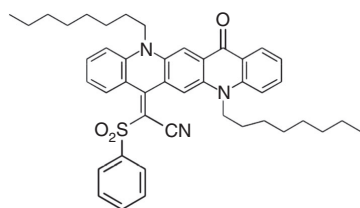


Chart 11.

Method B: 2-(Phenylsulfonyl)acetonitrile (0.36 g, 2 mmol) was reacted with **1b** (0.54 g, 1 mmol). The product was eluted from silica gel with 20 % light petroleum in DCM and crystallised from DCM/methanol to give **3d** (0.52 g, 74 % based on **1b**) as large, chunky needles, mp > 250°C.  $\delta_{\text{H}}$  8.76 (1H, s, ArH), 8.60 (1H, s, ArH), 8.59 (1H, m, ArH), 8.41 (1H, s, ArH), 7.2–7.9 (11H, m, 11ArH), 4.50 (2H, m, CH<sub>2</sub>N), 4.85 (2H, m, CH<sub>2</sub>N), 2.0 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.2–1.7 (8H, m, 4  $\times$  CH<sub>2</sub>), 0.89 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  (125.7 MHz, CDCl<sub>3</sub>) 177.5, 152.0, 142.2, 139.7, 139.3, 135.8, 134.6, 133.9, 133.4, 133.3, 129.6, 128.8, 128.6, 128.0, 125.0, 123.9, 121.2, 121.0, 120.7, 117.6, 117.5, 114.7, 113.3, 111.2, 47.6, 46.9, 31.8, 31.7, 29.3, 29.2, 27.3, 27.0, 26.8, 26.5, 22.7, 22.6, 14.1, 14.0.  $m/z$  699.3489; calcd for C<sub>44</sub>H<sub>49</sub>N<sub>3</sub>O<sub>3</sub>S 699.3495.

5-(5,12-Dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)-4-methyl-2,6-dioxo-1-phenyl-1,2,5,6-tetrahydropyridine-3-carbonitrile (**3e**) (Chart 12)

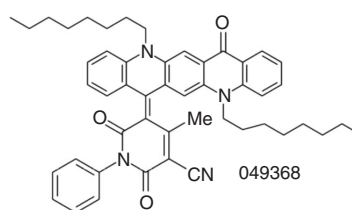


Chart 12.

Method B: The QA **1b** (1.0 g, 1.9 mmol) and the dioxypyridine<sup>[15]</sup> (1 g, 4.5 mmol) were reacted and worked up in the usual way. The organic phase was separated, the solvent removed by evaporation, and the residue was simmered with methanol (25 mL) for 5 min and cooled. The next day the solid was filtered off and purified by elution from a silica column with 5 % isopropyl alcohol/DCM and crystallised from DCM/ethanol to give **3e** (1.13 g, 81.3 % based on **1b**) as fine green needles, mp > 250°C.  $\delta_{\text{H}}$  9.40 (1H, s, ArH), 8.52 (3H, m, 3  $\times$  ArH), 8.20 (2H, br s, 2  $\times$  ArH), 7.87 (1H, m, ArH), 7.76 (1H, m, ArH), 7.55 (1H, d,  $J$  8.8, ArH), 7.2–7.4 (6H, m, 6  $\times$  ArH), 5.24 (2H, t,  $J$  7.1, CH<sub>2</sub>N), 4.30 (2H, t,  $J$  8.1, CH<sub>2</sub>N), 2.20 (2H, m, CH<sub>2</sub>), 1.94 (3H, s, =C–CH<sub>3</sub>), 1.95 (2H, m, CH<sub>2</sub>), 1.2–1.7 (16H, m, 8  $\times$  CH<sub>2</sub>), 0.85 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  (125.6 MHz, CDCl<sub>3</sub>) 177.7, 163.9, 162.9, 161.9, 153.5, 142.8, 140.8, 139.3, 138.9, 136.7, 136.4, 133.4, 132.1, 130.4, 129.6, 128.9, 128.8, 128.7, 128.4, 127.5, 127.2, 122.2, 121.0, 119.4, 116.9, 116.8, 115.0, 102.3, 84.0, 50.5, 47.0, 31.7, 31.6, 29.5, 29.2, 29.1, 29.1, 27.2, 27.0, 26.8, 22.6, 22.5, 22.5, 20.1, 14.1, 14.0.  $m/z$  744.4034; calcd for C<sub>49</sub>H<sub>52</sub>N<sub>4</sub>O<sub>3</sub> 744.4039.

#### Adducts Using an Activated –CH<sub>3</sub>

2,2'-(5,12-Dioctylquinolino[2,3-b]acridine-7,14 (5H,12H)-diylidene)bis(1-(3,4-dichlorophenyl)ethane-2,1-diylidene))dimalononitrile (**4a**) (Chart 13)

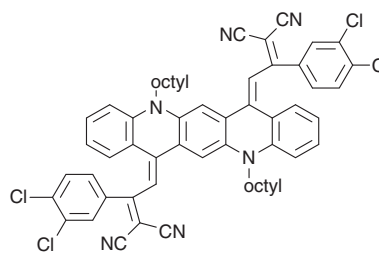


Chart 13.

Method D: To dioctylquinacridone **1b** (0.54 g, 1 mmol) in DCM (15 mL), was added  $\text{POCl}_3$  (0.60 g, 4 mmol) and 2,4,6-collidine (0.96 g, 8 mmol) at  $0^\circ\text{C}$  followed by the nitrile<sup>[16]</sup> (0.72 g, 3 mmol). The components were mixed and then allowed to react for 48 h before the mixture was worked up and purified by chromatography ( $\text{SiO}_2/\text{DCM}$ ), affording deep purple needles of **4a** from DCM/EtOAc (0.66 g, 82.6 % based on **1b**), mp  $>250^\circ\text{C}$ .  $\delta_{\text{H}}$  7.63 (4H, br s,  $2 \times \text{ArH}$  and  $2 \times \text{C}=\text{CH}$ ), 6.6–7.4 (16H, m,  $16 \times \text{ArH}$ ), 4.20 (4H, m,  $2 \times \text{CH}_2\text{N}$ ), 1.9 (4H, m,  $2 \times \text{CH}_2$ ), 1.3–1.6 (20H, m,  $10 \times \text{CH}_2$ ), 0.9 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  (125.8 MHz) 167.1, 146.9, 139.35, 135.2, 134.55, 133.3, 133.0, 132.4, 131.2, 130.9, 130.7, 128.8, 126.4, 121.45, 120.0, 115.6, 115.0, 114.9, 113.7, 109.8, 78.7, 47.4, 32.1, 32.00, 29.5, 29.4, 27.2, 26.9, 22.85, 14.3.  $m/z$  972.3002; calcd for  $\text{C}_{58}\text{H}_{52}\text{Cl}_4\text{N}_6$  972.3008.

2,2'-(5,12-Dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-diylidene)bis(1-(9H-fluoren-2-yl)ethane-2,1-diylidene))dimalononitrile (**4b**) (Chart 14)

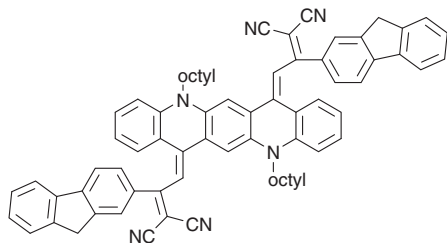


Chart 14.

Method A: The fluorene<sup>[17]</sup> (0.76 g, 3 mmol) and the QA **1b** were reacted. The mixture was worked up the next day and **4b** was eluted from silica (25 % light petroleum/DCM) and recrystallised from DCM/ethanol to give dark green prisms (0.62 g, 55 % from **1b**), mp  $234\text{--}236^\circ\text{C}$ .  $\delta_{\text{H}}$  7.48 (2H, br s,  $2 \times \text{C}=\text{CH}$ ), 7.0–7.5 (24H, m,  $24 \times \text{ArH}$ ), 4.18 (4H, br s,  $2 \times \text{CH}_2\text{N}$ ), 3.61 (4H, s,  $2 \times \text{ArCH}_2\text{Ar}$ ), 1.85–1.22 (24H, m,  $12 \times \text{CH}_2$ ), 0.88 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  170.0, 144.4, 143.3, 142.6, 139.8, 138.6, 131.0, 138.8, 128.2, 127.5, 126.7, 125.7, 124.7, 120.1, 119.3, 115.8, 115.2, 115.1, 46.7, 36.2, 31.4, 29.0, 28.9, 26.6, 26.2, 22.3, 13.7.  $m/z$  1012.5187; calcd for  $\text{C}_{72}\text{H}_{64}\text{N}_6$  1012.5192.

2,2'-(5,12-Dioctylquinolino[2,3-b]acridine-7,14(5H,12H)-diylidene)bis(1-(thiophen-3-yl)ethane-2,1-diylidene))dimalononitrile (**4c**) (Chart 15)

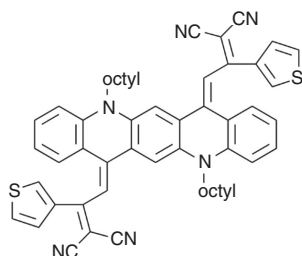


Chart 15.

Method D: 2-(1-(Thiophen-3-yl)ethylidene)malononitrile<sup>[18]</sup> (0.68 g, 4 mmol) was reacted with QA **1b** (0.54 g, 1 mmol). The mixture was worked up and **4c** was eluted from silica with 30 % light petroleum/DCM, and recrystallised from EtOH to give dendrites (0.40 g, 36 % based on **1b**), mp  $156\text{--}158^\circ\text{C}$ .  $\delta_{\text{H}}$  7.60 (4H, br s,  $4 \times \text{ArH}$ ), 7.36 (4H, m,  $2 \times \text{ArH}$ ), 7.17 (2H, m,

$2 \times \text{ArH}$ ), 6.94–7.17 (8H, m,  $8 \times \text{ArH}$ ), 6.81 (2H, s,  $2 \times \text{C}=\text{CH}$ ), 4.18 (4H, m,  $2 \times \text{CH}_2\text{N}$ ), 1.88 (4H, m,  $2 \times \text{CH}_2$ ), 1.30–1.60 (16H, m,  $8 \times \text{CH}_2$ ), 0.90 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  163.9, 145.5, 139.1, 134.6, 134.2, 131.5, 130.4, 127.7, 126.4, 121.0, 115.4, 115.2, 115.1, 113.3, 47.4, 31.7, 29.3, 29.2, 26.9, 26.5, 22.6, 14.1  $m/z$  848.3689; calcd for  $\text{C}_{54}\text{H}_{52}\text{N}_6\text{S}_2$  848.3695.

Adducts Using  $\text{R-NH}_2$

N-(5,12-dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)cyanamide (**5a**) (Chart 16)

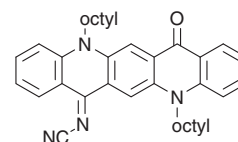


Chart 16.

Method B: The reaction was carried out with cyanamide (0.08 g, 2 mmol) and the QA **1b** (0.54 g, 1 mmol) and worked up in the usual way, purified on silica (DCM) and the residue was crystallised from DCM/ethanol to give **5a** as lustrous needles (0.41 g, 73 % based on **1b**), mp  $168\text{--}170^\circ\text{C}$ .  $\delta_{\text{H}}$  9.10 (2H, br m,  $2 \times \text{ArH}$ ), 8.68 (1H, s, ArH), 8.37 (1H, dd  $J$  1.5, 8, ArH), 7.78 (1H, m, ArH), 7.69 (1H, m, ArH), 7.54 (1H, d,  $J$  8.8, ArH), 7.45 (2H, d,  $J$  8.8,  $2 \times \text{ArH}$ ), 7.26 (1H, m, ArH), 7.13 (1H, m, ArH), 4.56 (2H, t,  $J$  7.9,  $\text{CH}_2\text{N}$ ), 4.44 (2H, t,  $J$  7.9,  $\text{CH}_2\text{N}$ ), 1.97 (4H, m,  $2 \times \text{CH}_2$ ), 1.67 (4H, m,  $2 \times \text{CH}_2$ ), 1.2–1.5 (16H, m,  $8 \times \text{CH}_2$ ), 0.90 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  (125.7 MHz,  $\text{CDCl}_3$ ) 177.7, 164.2, 142.4, 140.55, 136.05, 135.5, 135.1, 133.8, 128.0, 127.7, 126.7, 124.7, 122.0, 121.2, 121.1, 120.1, 118.0, 115.25, 115.0, 113.95, 112.8, 47.6, 46.8, 32.0, 32.0, 29.6, 29.6, 29.45, 27.45, 27.2 ( $2 \times \text{C}$ ), 27.0, 22.9, 22.8, 14.3 ( $2 \times \text{C}$ ).  $m/z$  560.3510; calcd for  $\text{C}_{37}\text{H}_{44}\text{N}_4\text{O}$  560.3515.

4-Chloro-N-(5,12-dioctyl-14-oxoquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)benzenesulfonamide (**5b**) (Chart 17)

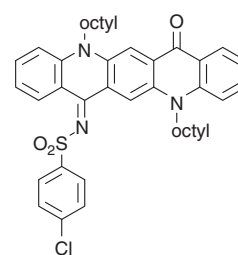


Chart 17.

Method D: 4-Chlorobenzenesulfonamide (0.29 g, 1.5 mmol) was reacted with QA **1b** (0.54 g, 1 mmol) in the usual way and after work up and chromatography (silica/chloroform) gave **5b** as purple flat needles from DCM/ethanol (0.51 g, 72 % based on **1b**), mp  $193\text{--}195^\circ\text{C}$ .  $\delta_{\text{H}}$  9.18 (1H, s, ArH), 8.77 (1H, s, ArH), 8.72 (1H, dd,  $J$  8.4, 1.5, ArH), 8.48 (1H, dd,  $J$  8.0, 1.7, ArH), 8.07 (2H, m,  $2 \times \text{ArH}$ ), 7.70 (2H, m,  $2 \times \text{ArH}$ ), 7.48 (4H, m,  $4 \times \text{ArH}$ ), 7.23 (2H, m, ArH), 4.58 (2H, t,  $J$  8.2,  $\text{NCH}_2$ ), 4.42 (2H, t,  $J$  8.2,  $\text{NCH}_2$ ), 1.95 (4H, m,  $2 \times \text{CH}_2$ ), 1.2–1.7 (20H, m,  $10 \times \text{CH}_2$ ), 0.88 (6H, m,  $2 \times \text{CH}_3$ ).  $\delta_{\text{C}}$  179.3, 162.7, 145.3, 144.0, 142.8, 139.1, 137.6, 136.7, 136.5, 136.2, 131.6, 130.4, 129.55, 129.2, 128.2, 125.3, 123.5, 122.6, 122.5, 121.3, 118.2,

116.3, 116.15, 114.9, 49.2, 48.4, 33.4, 33.3, 30.94, 30.88, 30.87, 30.85, 28.9, 28.6, 28.4, 28.3, 24.2, 24.2, 15.7, 14.7.  $m/z$  709.3099; calcd for  $C_{42}H_{48}ClN_3O_3S$  709.3105.

*N*-(5,12-Dioctyl-14-oxoquinolino[2,3-*b*]acridin-7(5*H*,12*H*,14*H*)-ylidene)piperidine-1-carboxamide (**5c**) (Chart 18)

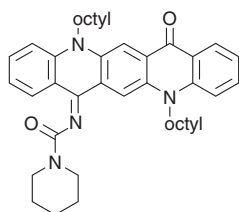


Chart 18.

Method B: A reaction between piperidine-1-carboxamide (0.26 g, 2 mmol) and QA **1b** (0.54 g, 1 mmol) was followed by chromatography and recrystallisation from methanol and gave **5c** as red plates (0.44 g, 68 % based on **1b**), mp 153–155°C.  $\delta_H$  (8.68 (1*H*, s, ArH), 8.50 (1*H*, dd,  $J$  1.7, 8.0, ArH), 8.49 (1*H*, s, ArH), 8.17 (1*H*, dd,  $J$  1.6, 8.2, ArH), 7.63 (1*H*, m, ArH), 7.54 (1*H*, m, ArH), 7.47 (1*H*, d,  $J$  8.7, ArH), 7.31 (1*H*, d,  $J$  8.6, ArH), 7.18 (1*H*, m, ArH), 7.09 (1*H*, m, ArH), 4.41 (2*H*, t,  $J$  8.1,  $CH_2N$ ), 4.28 (2*H*, t,  $J$  8.2,  $CH_2N$ ), 3.73 (2*H*, t,  $J$  5.4,  $CH_2NCH_2$ ), 3.28 (2*H*, t,  $J$  5.4,  $CH_2NCH_2$ ), 1.92 (4*H*, m,  $2 \times CH_2$ ), 1.2–1.7 (20*H*, m,  $10 \times CH_2$ ), 0.86 (6*H*, m,  $2 \times CH_3$ ).  $\delta_C$  (125.7 MHz,  $CDCl_3$ ) 178.05, 164.2, 152.85, 142.3, 141.25, 136.1, 135.1, 134.5, 133.2, 128.5, 128.2, 126.2, 125.4, 121.4, 120.9, 120.8, 118.1, 114.8, 114.6, 113.8, 112.2, 47.0, 46.53, 46.50, 43.7, 32.00, 31.98, 29.65, 29.6 (2  $\times$  C), 29.5, 27.4, 27.23, 27.20, 26.8, 26.1, 25.9, 24.85, 22.83 (2  $\times$  C), 14.3 (2  $\times$  C).  $m/z$  646.4241; calcd for  $C_{42}H_{54}N_4O_2$  646.4247.

#### Condensations of QA Malononitrile Mono-Condensation Product **3b** with a Second Reactant

Methyl 2-Cyano-2-(14-(dicyanomethylene)-5,12-dioctylquinolino[2,3-*b*]acridin-7(5*H*,12*H*,14*H*)-ylidene)acetate (**6a**) (Chart 19)

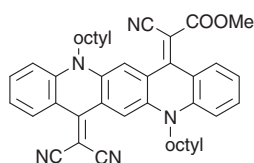


Chart 19.

Method C: Methyl cyanoacetate (0.20 g, 2 mmol) was reacted with the QA **3b** (0.58 g, 1 mmol). Compound **6a** was eluted with DCM containing up to 20 % light petroleum and crystallised from DCM/methanol to give green needles (0.41 g, 62 % based on **3b**), mp 172–174°C.  $\delta_H$  8.59 (1*H*, d,  $J$  8.0, ArH), 8.51 (1*H*, s, ArH), 7.74 (1*H*, m, ArH), 7.63 (1*H*, m, ArH), 7.49 (1*H*, d,  $J$  8.7, ArH), 7.38 (1*H*, d,  $J$  8.6, ArH), 7.31 (1*H*, m, ArH), 7.17 (1*H*, m, ArH), 4.45 (2*H*, t,  $J$  6.4,  $CH_2N$ ), 4.38 (2*H*, t,  $J$  8.1,  $CH_2N$ ), 3.85 (3*H*, s,  $CH_3O$ ), 2.03 (4*H*,  $2 \times CH_2$ ), 1.65 (4*H*, m,  $4 \times ArH$ ), 1.50 (4*H*, m,  $4 \times ArH$ ), 1.3–1.4 (12*H*, m,  $6 \times CH_2$ ), 0.93 (6*H*, m,  $2 \times CH_3$ ).  $\delta_C$  (125.7 MHz) 166.5, 156.7, 141.2, 140.7, 135.6, 134.8, 134.6, 128.8, 123.2, 123.0, 122.4, 121.0,

119.4, 118.9, 118.7, 116.0, 115.6, 112.1, 70.2, 54.4, 50.5, 50.3, 33.3, 33.3, 30.8, 30.8, 28.6, 28.4, 28.2, 24.2 15.7.  $m/z$  665.3724; calcd for  $C_{43}H_{47}N_5O_2$  665.3730.

2-(14-(1-Cyano-2-oxo-2-(pyrrolidin-1-yl)ethylidene)-5,12-dioctylquinolino[2,3-*b*]acridin-7(5*H*,12*H*,14*H*)-ylidene)malononitrile (**6b**) (Chart 20)

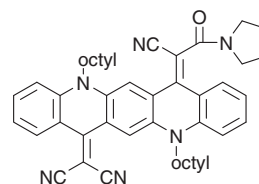


Chart 20.

Method C: 3-Oxo-3-(pyrrolidin-1-yl)propanenitrile<sup>[19]</sup> (0.28 g, 2 mmol) was reacted with QA **3b** (0.58 g, 1 mmol). Compound **6b** was eluted with DCM containing up to 2 % ethyl acetate and crystallised from DCM/cyclohexane as granules (0.44 g, 62.4 % from **3b**), mp 155–157°C.  $\delta_H$  (2 % trifluoroacetic acid in  $CDCl_3$ ) 8.59 (H, dd,  $J$  1.3, 8.4, ArH), 8.53 (H, s, ArH), 8.48 (H, s, ArH), 7.75 (2*H*, m,  $2 \times ArH$ ), 7.57 (2*H*, m,  $2 \times ArH$ ), 7.36 (2*H*, m,  $2 \times ArH$ ), 7.14 (H, t,  $J$  7.1, ArH), 4.47 (2*H*, m,  $CH_2N$ ), 4.31 (2*H*, m,  $CH_2N$ ), 3.57 (2*H*, m,  $CH_2NCO$  (restricted rotation)), 2.88 (2*H*, m,  $CH_2N(CO)H_2C$  (restricted rotation)), 2.05 (2*H*, m,  $CH_2$ ), 1.94 (2*H*, m,  $CH_2$ ), 1.79 (2*H*, m,  $CH_2$ ), 1.70 (2*H*, m,  $CH_2$ ), 1.25–1.50 (20*H*, m,  $10 \times CH_2$ ), 0.88 (6*H*, m,  $2 \times CH_3$ ).  $\delta_C$  (125.7 MHz) 177.8, 159.9, 155.1, 146.7, 142.3, 141.35, 136.25, 135.0, 134.7, 134.3, 128.1, 127.95, 126.4, 125.3, 124.8, 121.6, 121.2 (2  $\times$  C), 116.6, 115.7, 114.8, 113.6 (2  $\times$  C), 111.9, 109.2, 107.2, 66.0, 47.4, 46.4, 32.0, 31.85, 29.6, 29.52, 29.46 (2  $\times$  C), 27.3, 27.1, 27.1 (2  $\times$  C), 22.8 (2  $\times$  C), 14.28, 14.27, 13.8.  $m/z$  704.4197, calcd for  $C_{46}H_{52}N_6O$  704.4203.

2-(14-(Cyano(phenylsulfonyl)methylene)-5,12-dioctylquinolino[2,3-*b*]acridin-7(5*H*,12*H*,14*H*)-ylidene)malononitrile (**6c**) (Chart 21)

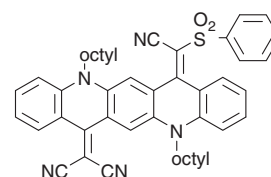


Chart 21.

Method C: 2-(Phenylsulfonyl)acetonitrile<sup>[20]</sup> (0.36 g, 2 mmol) was reacted with QA **3b** (0.58 g, 1 mmol). Compound **6c** was eluted with DCM and crystallised from methanol to give dark flocs (0.52 g, 70 % based on **3b**), mp 170–172°C.  $\delta_H$  8.62 (H, s, ArH), 8.59 (H d,  $J$  8.3, ArH), 8.42 (H, s, ArH), 8.40 (H, d,  $J$  8.3, ArH), 7.30–7.80 (12*H*, m,  $12 \times ArH$ ), 4.45, 4.34 (2*H*, 2*H*, m,  $2 \times CH_2N$ ), 1.95 (4*H*, m,  $2 \times CH_2$ ), 1.6 (4*H*, m,  $2 \times CH_2$ ), 1.23–1.5 (20*H*, m,  $10 \times CH_2$ ), 0.88 (6*H*, m,  $2 \times CH_3$ ).  $\delta_C$  154.9, 150.8, 139.1, 138.9, 138.5, 133.9, 133.8, 133.4, 133.2, 132.7, 128.5, 128.3, 126.8, 121.5, 121.3, 120.8, 117.4, 117.05, 116.8, 116.7, 114.1, 113.2, 109.8, 48.4, 48.3, 31.4, 28.9, 28.85, 26.65, 26.5, 26.4, 26.4, 22.31, 22.29, 13.75.  $m/z$  747.3601; calcd for  $C_{47}H_{49}N_5O_2S$  747.3607.



2-(14-(1-Cyano-2-oxo-2-phenylethylidene)-5,12-dioctylquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)malononitrile (**6d**) (Chart 22)

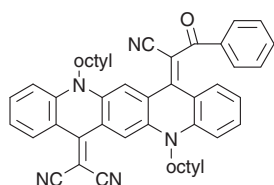


Chart 22.

Method C: Benzoylacetonitrile (0.29 g, 2 mmol) was reacted with QA **3b** (0.58 g, 1 mmol). Compound **6d** was eluted with 5 % ethyl acetate/DCM and crystallised from ethanol to give blue needles (0.44 g, 66 % from **3b**), mp 172–174°C.  $\delta_{\text{H}}$  8.77 (H, s, ArH), 8.71 (H, s, ArH), 8.52 (H, d, *J* 8.4, ArH), 7.85 (H, d, *J* 8.3, ArH), 7.2–7.7 (11H, m, 11  $\times$  ArH), 4.50 (2H, m, CH<sub>2</sub>N), 4.40 (2H, m, 2  $\times$  CH<sub>2</sub>N), 2.0 (4H, m, 2  $\times$  CH<sub>2</sub>), 1.2–1.7 (20H, m, 10  $\times$  CH<sub>2</sub>), 0.87 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  (125.7 MHz) 170.2, 155.1, 152.7, 139.7, 139.3, 134.6, 134.5, 134.34, 134.29, 133.7, 132.9, 130.0, 129.1, 129.0, 127.2, 125.5, 123.3, 122.9, 122.1, 120.2, 199.9, 117.4, 117.2, 116.6, 115.2, 114.61, 114.57, 112.4, 111.9, 77.2, 49.2, 49.1, 31.8, 31.7, 29.24, 29.21, 29.18, 27.36, 27.0, 26.9, 26.8, 22.7, 22.6, 14.1 (2  $\times$  C). 192.1, 155.4, 149.0, 139.7, 139.1, 135.55, 134.4, 134.2, 134.05, 133.7, 132.8, 129.2, 128.95, 128.8, 127.3, 125.6, 121.8, 121.5, 121.4, 119.3, 118.8, 118.1, 117.5, 117.4, 114.6, 113.8, 112.5, 110.7, 102.2, 68.6, 49.0, 48.5, 31.95, 29.45 (2  $\times$  C), 29.4 (2  $\times$  C), 27.3, 27.0 (2  $\times$  C), 27.0, 26.7, 22.85, 22.8, 14.3 (2  $\times$  C). *m/z* 711.3932; calcd for C<sub>48</sub>H<sub>49</sub>N<sub>5</sub>O 711.3937.

2,2'-(2-(14-(Dicyanomethylene)-5,12-dioctylquinolino[2,3-b]acridin-7(5H,12H,14H)-ylidene)-1H-indene-1,3(2H)-diylidene)dimalononitrile (**6e**) (Chart 23)

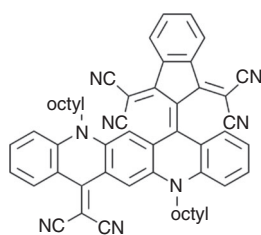


Chart 23.

Method D: 2,2'-(1H-Indene-1,3(2H)-diylidene)dimalononitrile<sup>[21]</sup> (0.48 g, 2 mmol) was reacted with QA **3b** (0.58 g, 1 mmol). Compound **6e** was eluted with DCM containing up to 2 % ethyl acetate and crystallised from DCM/ethanol to afford a dark powder (0.68 g, 84.1 % from **3b**), mp > 250°C.  $\delta_{\text{H}}$  9.50 (1H, s, ArH), 8.51 (3H, m, 3  $\times$  ArH), 8.28 (3H, m, 3  $\times$  ArH), 8.11 (1H, s, ArH), 7.84 (2H, m, 2  $\times$  ArH), 7.55 (2H, m, 2  $\times$  ArH), 7.48 (1H, d, *J* 8.6, ArH), 7.42 (1H, m, ArH), 5.30 (2H, t, *J* 8.2, CH<sub>2</sub>N), 4.24 (2H, t, *J* 8.6, CH<sub>2</sub>N), 2.30 (2H, m, CH<sub>2</sub>), 1.91 (2H, m, CH<sub>2</sub>), 1.75 (2H, m, CH<sub>2</sub>), 1.53 (2H, m, CH<sub>2</sub>), 1.05–1.45 (16H, m, 8  $\times$  CH<sub>2</sub>), 0.92 (6H, m, 2  $\times$  CH<sub>3</sub>).  $\delta_{\text{C}}$  (125.7 MHz) 156.4, 156.0, 154.9, 139.9, 139.2, 139.1, 137.1, 136.5, 135.3, 132.6, 130.8, 130.5, 130.3, 130.2, 128.4, 128.0, 127.25, 123.1, 122.6, 117.3, 117.0, 116.4, 116.3, 116.0, 115.9, 114.9, 114.1, 111.2, 103.8,

77.0, 54.2, 51.1, 48.8, 31.3, 31.2, 29.1, 28.9, 28.80, 28.69, 26.7, 26.6, 25.3, 22.3, 22.25, 13.8, 13.7. *m/z* 808.3996; calcd for C<sub>54</sub>H<sub>48</sub>N<sub>8</sub> 808.4002.

### X-Ray Crystallography

Crystals were mounted on fine glass fibres using viscous hydrocarbon oil. Data were collected on a Bruker X8 Apex II CCD Diffractometer (**3d**, **4c**, **5a**, **6a**) (Mo K $\alpha$  radiation,  $\lambda$  0.71073 Å, 123 K) or on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron (**2b**, **5b**) ( $\lambda$  0.710900 Å, 100 K). Data collection temperatures were maintained using an open flow N<sub>2</sub> cryostream. Solutions were obtained by direct methods or Patterson synthesis using *SHELXS* 97<sup>[22]</sup> followed by successive refinements using full matrix least-squares method against F<sup>2</sup> using *SHELXL* 97.<sup>[22]</sup> The data collection and integration at the Australian Synchrotron were performed within *Blu-Ice*<sup>[23]</sup> and *XDS* software programs.<sup>[24]</sup> The program *X-Seed* was used as a graphical *SHELX* interface.<sup>[25]</sup> All datasets were treated for the effects of absorption. CCDC 1847848 (**2b**), CCDC 1847849 (**3d**), CCDC 1847850 (**4c**), CCDC 1847851 (**5a**), CCDC 1847852 (**5b**), CCDC 1874853 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Crystal data for **2b**: C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>, *M* 330.44, red block, 0.1  $\times$  0.1  $\times$  0.1 mm<sup>3</sup>, triclinic, space group *P*-1, *V* 894.4(4) Å<sup>3</sup>, *Z* 2, *D*<sub>c</sub> 1.227 g cm<sup>-3</sup>, *F*<sub>000</sub> 354, 2 $\theta$ <sub>max</sub> 55.0°, 7599 reflections collected, 3731 unique (*R*<sub>int</sub> 0.0315). Final *GooF* 1.055, *R*<sub>1</sub> 0.0510, *wR*<sub>2</sub> 0.1376, *R* indices based on 3134 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 228 parameters, 0 restraints.

Crystal data for **3d**: C<sub>44</sub>H<sub>49</sub>N<sub>3</sub>O<sub>3</sub>S, *M* 699.92, red plate, 0.5  $\times$  0.4  $\times$  0.2 mm<sup>3</sup>, monoclinic, space group *P*2<sub>1</sub>/*n*, *V* 3603.9(3) Å<sup>3</sup>, *Z* 4, *D*<sub>c</sub> 1.290 g cm<sup>-3</sup>, *F*<sub>000</sub> 1496, 2 $\theta$ <sub>max</sub> 55.0°, 41054 reflections collected, 8263 unique (*R*<sub>int</sub> 0.0210). Final *GooF* 1.058, *R*<sub>1</sub> 0.0460, *wR*<sub>2</sub> 0.1200, *R* indices based on 7405 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 462 parameters, 0 restraints.

Crystal data for **4c**: C<sub>27</sub>H<sub>26</sub>N<sub>3</sub>S, *M* 424.57, green flat needle, 0.4  $\times$  0.2  $\times$  0.1 mm<sup>3</sup>, monoclinic, space group *P*2<sub>1</sub>/*n*, *V* 2237.4(2) Å<sup>3</sup>, *Z* 4, *D*<sub>c</sub> 1.260 g cm<sup>-3</sup>, *F*<sub>000</sub> 900, 2 $\theta$ <sub>max</sub> 55.0°, 17398 reflections collected, 5099 unique (*R*<sub>int</sub> 0.0257). Final *GooF* 1.035, *R*<sub>1</sub> 0.0618, *wR*<sub>2</sub> 0.1632, *R* indices based on 3414 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 309 parameters, 0 restraints. A portion of the octyl group is disordered over two positions, with the site occupancies refined against each other (53 : 44).

Crystal data for **5a**: C<sub>37</sub>H<sub>44</sub>N<sub>4</sub>O, *M* 560.76, red plate, 0.3  $\times$  0.3  $\times$  0.0 mm<sup>3</sup>, triclinic, space group *P*-1, *V* 771.02(10) Å<sup>3</sup>, *Z* 1, *D*<sub>c</sub> 1.208 g cm<sup>-3</sup>, *F*<sub>000</sub> 302, 2 $\theta$ <sub>max</sub> 55.0°, 5730 reflections collected, 3500 unique (*R*<sub>int</sub> 0.0195). Final *GooF* 1.024, *R*<sub>1</sub> 0.0606, *wR*<sub>2</sub> 0.1508, *R* indices based on 2395 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 209 parameters, 0 restraints.

Crystal data for **5b**: C<sub>42</sub>H<sub>48</sub>ClN<sub>3</sub>O<sub>3</sub>S, *M* 710.34, red block, 0.1  $\times$  0.1  $\times$  0.1 mm<sup>3</sup>, triclinic, space group *P*-1, *V* 1790.0(6) Å<sup>3</sup>, *Z* 2, *D*<sub>c</sub> 1.318 g cm<sup>-3</sup>, *F*<sub>000</sub> 756, 2 $\theta$ <sub>max</sub> 55.0°, 15078 reflections collected, 7451 unique (*R*<sub>int</sub> 0.0634). Final *GooF* 0.965, *R*<sub>1</sub> 0.0606, *wR*<sub>2</sub> 0.1501, *R* indices based on 4844 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 453 parameters, 0 restraints.

Crystal data for **6a**: C<sub>43</sub>H<sub>47</sub>N<sub>5</sub>O<sub>2</sub>, *M* 665.85, blue plate, 0.8  $\times$  0.8  $\times$  0.1 mm<sup>3</sup>, monoclinic, space group *C*2/*c*, *V* 7387.8(8) Å<sup>3</sup>, *Z* 8, *D*<sub>c</sub> 1.197 g cm<sup>-3</sup>, *F*<sub>000</sub> 2848, 2 $\theta$ <sub>max</sub> 55.0°, 25415 reflections collected, 8432 unique (*R*<sub>int</sub> 0.0521). Final *GooF* 1.024, *R*<sub>1</sub> 0.0642, *wR*<sub>2</sub> 0.1517, *R* indices based on 5073 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 465 parameters, 0



restraints. A portion of an octyl group is disordered over two positions, with the site occupancies refined against each other (72 : 28).

### Supplementary Material

<sup>1</sup>H and <sup>13</sup>C NMR spectra of characterised materials are available on the Journal's website.

### Conflicts of Interest

The authors declare no conflicts of interest.

### Acknowledgements

This research was undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO. The authors thank Dr Roger Mulder and Dr Jo Cosgriff for assistance with NMR spectroscopy, and Mr Carl Braybrook and Dr Jo Cosgriff for mass spectrometry. This research did not receive any specific funding.

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