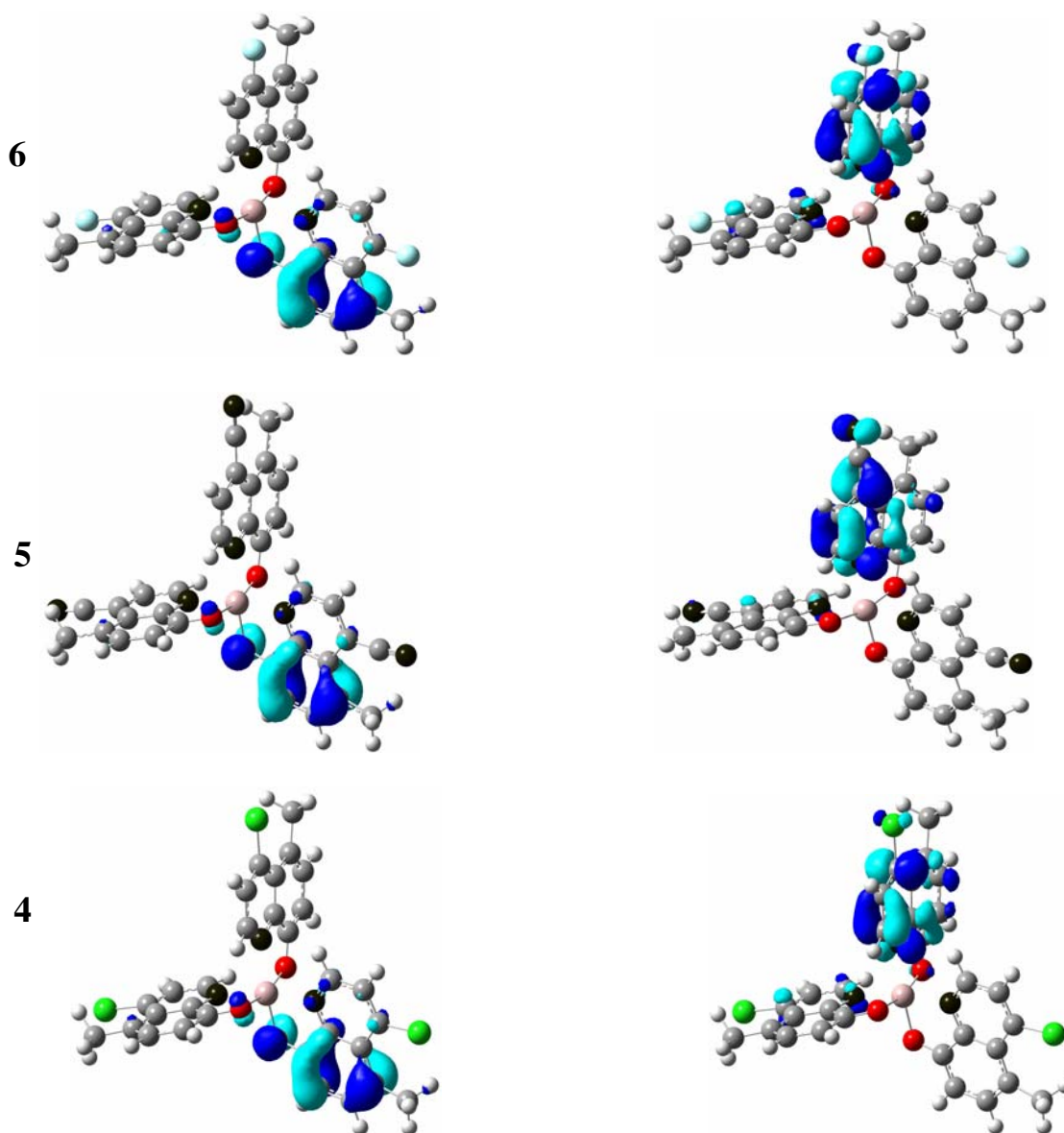**Supplementary Materials**

Designing of disubstituted derivatives of *mer*-Alq3: Quantum theoretical study

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Punjab, Pakistan; Currently at Subsurface Technology, Petronas Research Sdn Bhd.

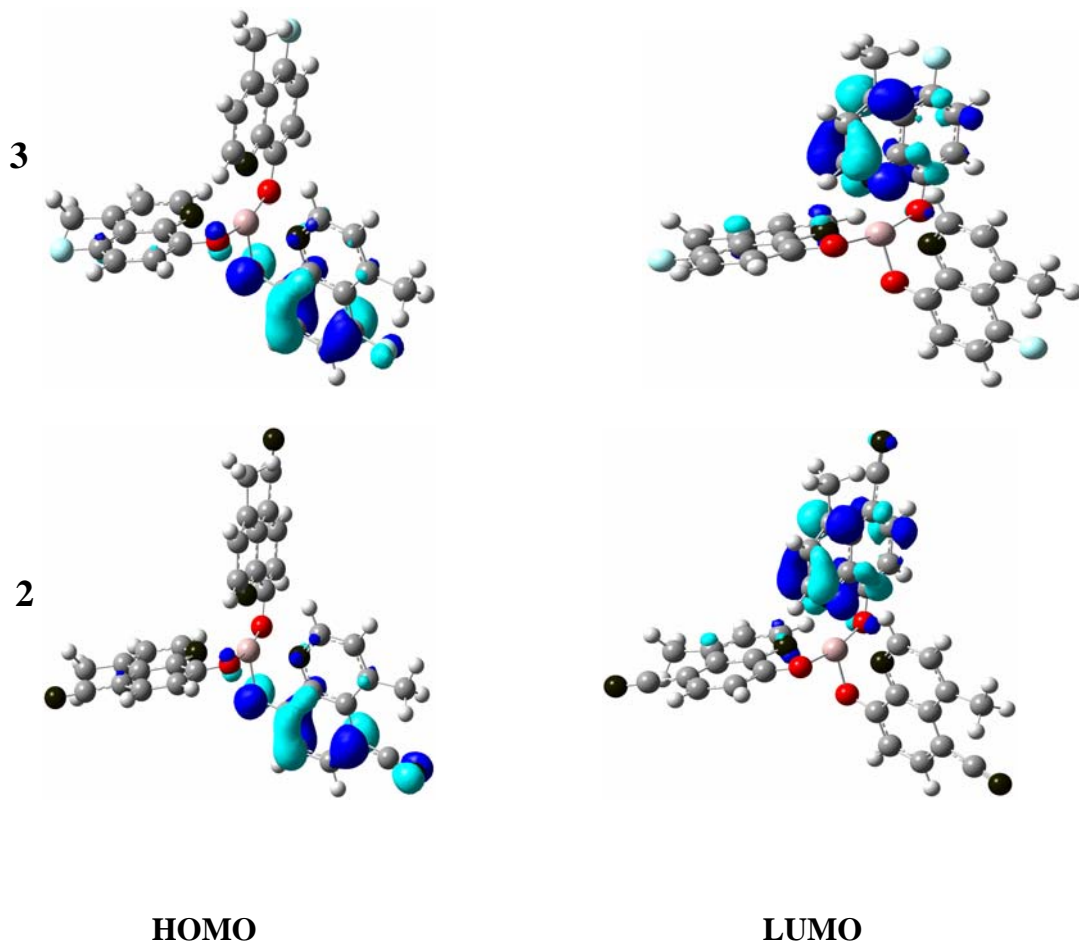(PRSB), Bangi-43300, Selangor, Malaysia

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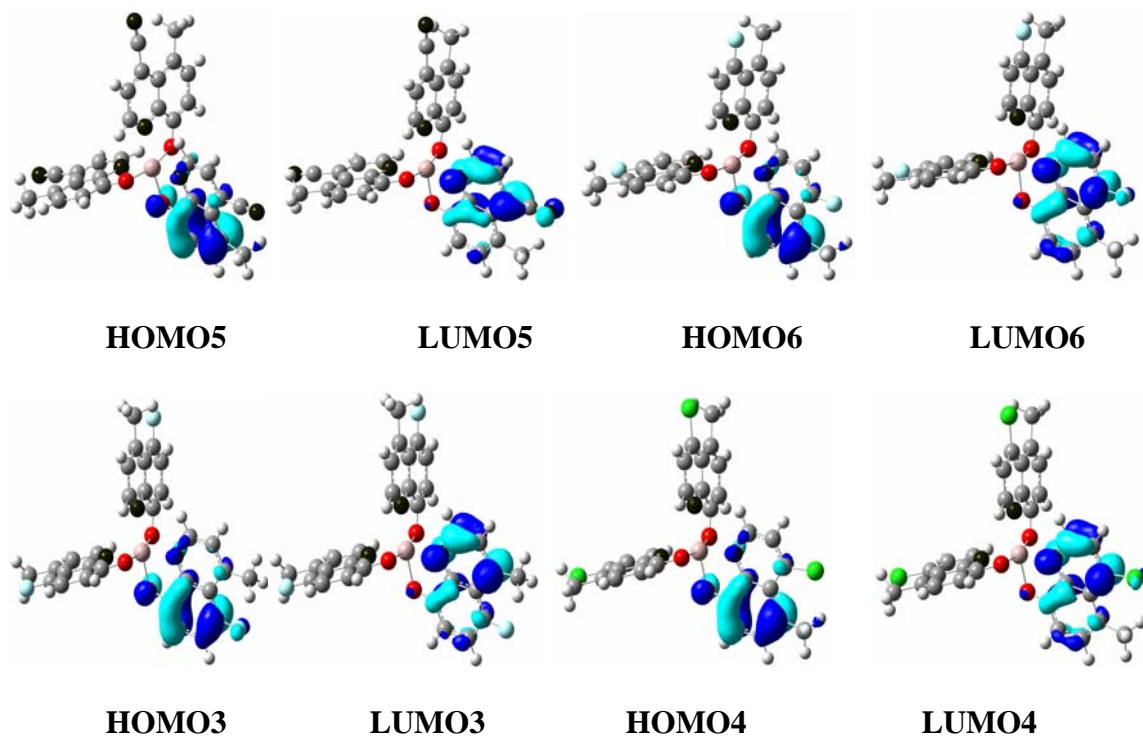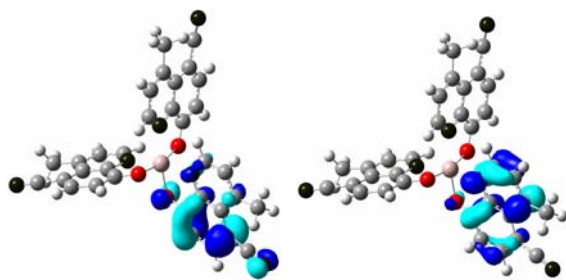**HOMO**   **LUMO**

Fig. S1. Frontier molecular orbitals (FMOs) (0.05 e au^{-3}) for the ground states (S$_0$) of disubstituted derivatives of *mer*-Alq3.

HOMO5   **LUMO5**   **HOMO6**   **LUMO6**

HOMO3   **LUMO3**   **HOMO4**   **LUMO4**

HOMO2   **LUMO2**

Fig. S2. Frontier molecular orbitals (FMOs) (0.05 e au^{-3}) for the excited states (S$_1$) of disubstituted derivatives of *mer*-Alq3.

Theoretical background of bond dissociation energy

        The over all bond energy ΔE is divided into two major components [eq. 1]. The preparation energy ΔE_{prep} corresponding to the amount of energy required to deform the separated fragments, from their equilibrium structure to the geometry they acquire in the overall molecule ($\Delta E_{prep,\ geo}$), and to excite them to their valence electronic configuration ($\Delta E_{prep,\ el}$). In the second term, the interaction energy ΔE_{int} between the prepared fragments.

$$\Delta E = \Delta E_{prep} + \Delta E_{int} = \Delta E_{prep,\ geo} + \Delta E_{prep,\ el} + \Delta E_{int} \qquad (1)$$

The interaction energy ΔE_{int} is further decomposed into three physically meaningful terms.

$$\Delta E_{int} = \Delta E_{elst} + \Delta E_{pauli} + \Delta E_{oi} \qquad (2)$$

The term ΔE_{elst} is associated with the electrostatic interaction between the unperturbed charge distributions of the prepared fragments as they are brought together at their final positions, yielding the overall density that is simply a superposition of fragment densities $\rho_A + \rho_B$. The repulsive term ΔE_{pauli} is caused by going from the product of fragment wave functions ψ_A and ψ_B to $\psi^0 = NA[\psi_A\psi_B]$ that properly obeys the Pauli principle (A - antisymmetrization operator, N - renormalization constant). The orbital interaction energy ΔE_{oi} is the energy change due to the relaxation of the wave function to its final form

through electron pair bonding, charge transfer and polarization. The orbital term ΔE_{oi} can be considered as an estimate of the covalent contributions to the attractive interactions. Thus, the ratio $\Delta E_{elst}/\Delta E_{oi}$ indicates the electrostatic/covalent character of the bond.

Table S1
Selected optimized bond angles (degree) for *mer*-Alq3 and its disubstituted derivatives at the B3LYP/6-31G* Level

Complexes	N_A–Al–N_C	N_B–Al–O_A	O_C–Al–O_B
Alq3	171.53	172.57	166.56
1	170.59	171.98	166.00
2	170.41	172.12	167.00
3	171.14	172.31	166.07
4	170.48	172.03	165.51
5	170.60	172.42	165.48
6	170.98	172.33	166.01
Exp[A]	173.82	171.46	168.22

[A]Experimental data of *mer*-Alq3 from ref. S36

Optical properties

As for the electronic excited states, the focus was mainly on the properties of the $S_1 \rightarrow S_0$ transition, as Alq_3 is the so-called singlet emitter. The reviewer draws our attention toward this issue thus we have calculated the triplet emissions of Alq3 and its derivatives. We observed that the oscillator strength in triplet emission is zero in parent molecule as well as studied systems. We presented this data in supporting information and explained in our revised manuscript. If we neglect the oscillator strength, we have observed interesting feature that triplet state energies are lower than the singlet state ones. By considering singlet emitter energies of the maximum oscillator strength in *mer*-Alq3,**1**, **2**, **3**, **4**, **5**, and **6** are 2.4506 eV, 2.4572 eV, 2.6791 eV, 2.3360 eV, 2.2998 eV, 1.7749 eV, 2.4963 eV which are higher than the triplet for the same excited states, i.e., 1.8278 eV, 1.8801 eV, 2.0631 eV, 1.9202 eV, 1.7437 eV, 1.2860 eV, 2.0127 eV, respectively. Our computed triplet emission for Alq3 is 678 nm which is in good agreement with Burrow et al. whom observed broad band emission at 660 nm and assigned to Alq3 phosphorescence.

Alq3-triplet

Excited State   1:   Triplet-A   0.8020 eV 1545.91 nm   f=0.0000
         119 ->120   0.70716

Excited State   2:   Triplet-A   1.7085 eV   725.70 nm   f=0.0000
    106 ->120   -0.11428
    117 ->120   0.76483
    117 ->125   -0.12180

Excited State   3:   Triplet-A   1.7328 eV   715.50 nm   f=0.0000
    119 ->121   -0.19536
    119 ->123   0.74167
    119 ->129   -0.12804

Excited State   4:   Triplet-A   1.8278 eV   678.31 nm   f=0.0000
    119 ->121   0.67295
    119 ->123   0.20814

Excited State   5:   Triplet-A   1.9662 eV   630.58 nm   f=0.0000
    118 ->120   0.67384
    118 ->121   -0.21898

Alq3-singlet

Excited State   1:   Singlet-A   0.8034 eV 1543.28 nm   f=0.0001
    119 ->120   0.70688

Excited State   2:   Singlet-A   1.8345 eV   675.86 nm   f=0.0025
    119 ->121   0.70661

Excited State   3:   Singlet-A   1.9953 eV   621.39 nm   f=0.0013
    118 ->120   0.70644

Excited State   4:   Singlet-A   2.4506 eV   505.94 nm   f=0.0393
    117 ->120   0.56670
    119 ->123   -0.41410

Excited State   5:   Singlet-A   2.4828 eV   499.37 nm   f=0.0306
    117 ->120   0.40625
    119 ->123   0.56361

1-triplet

Excited State   1:   Triplet-A   0.9215 eV 1345.41 nm   f=0.0000
        155 ->156   0.70675

 Excited State   2:   Triplet-A   1.7203 eV   720.71 nm   f=0.0000
        153 ->156   0.68758

 Excited State   3:   Triplet-A   1.7339 eV   715.06 nm   f=0.0000
        155 ->157   -0.16836
        155 ->159   0.67203

 Excited State   4:   Triplet-A   1.8801 eV   659.46 nm   f=0.0000
        154 ->157   0.12249
        155 ->157   0.67056
        155 ->159   0.16467

 Excited State   5:   Triplet-A   1.9986 eV   620.37 nm   f=0.0000
        154 ->156   0.64475
        154 ->157   -0.25229
        155 ->157   0.11605

1-singlet

Excited State   1:   Singlet-A   0.9235 eV 1342.61 nm   f=0.0003
        155 ->156   0.70649

 Excited State   2:   Singlet-A   1.8896 eV   656.14 nm   f=0.0048
        155 ->157   0.70543

 Excited State   3:   Singlet-A   2.0373 eV   608.59 nm   f=0.0024
        154 ->156   0.70533

 Excited State   4:   Singlet-A   2.4572 eV   504.58 nm   f=0.0461
        153 ->156   0.52039
        155 ->158   -0.25629
        155 ->159   -0.33352

Excited State   5:   Singlet-A   2.4740 eV   501.15 nm   f=0.0176
    153 ->156   0.22200
    155 ->158   0.65727

2-triplet

Excited State   1:   Triplet-A   1.1442 eV 1083.55 nm   f=0.0000
    149 ->150   0.70668

Excited State   2:   Triplet-A   1.8237 eV   679.87 nm   f=0.0000
    147 ->150   0.68732

Excited State   3:   Triplet-A   1.9231 eV   644.72 nm   f=0.0000
    149 ->151   -0.17869
    149 ->153   0.66585

Excited State   4:   Triplet-A   2.0631 eV   600.97 nm   f=0.0000
    148 ->150   -0.12858
    148 ->151   0.21225
    149 ->151   0.63592
    149 ->153   0.16931

Excited State   5:   Triplet-A   2.1488 eV   576.99 nm   f=0.0000
    148 ->150   0.55639
    148 ->151   -0.35481
    149 ->151   0.22753

2-singlet

Excited State   1:   Singlet-A   1.1461 eV 1081.75 nm   f=0.0003
    149 ->150   0.70656
Excited State   2:   Singlet-A   2.0770 eV   596.94 nm   f=0.0047
    149 ->151   0.70561

Excited State   3:   Singlet-A   2.2027 eV   562.86 nm   f=0.0022

148 ->150   0.70544

Excited State   4:   Singlet-A   2.6791 eV   462.79 nm   f=0.0868
   147 ->150   0.59048
   149 ->152   0.10319
   149 ->153   -0.26653

Excited State   5:   Singlet-A   2.7232 eV   455.28 nm   f=0.0252
   147 ->150   -0.21331
   149 ->152   0.58854
   149 ->153   -0.28352

3-triplet

Excited State   1:   Triplet-A   0.7482 eV 1657.12 nm   f=0.0000
   143 ->144   0.70724

Excited State   2:   Triplet-A   1.6174 eV   766.58 nm   f=0.0000
   143 ->145   -0.19727
   143 ->147   0.74580
   143 ->153   -0.13546

Excited State   3:   Triplet-A   1.6755 eV   739.98 nm   f=0.0000
   131 ->144   -0.10031
   141 ->144   0.76766
   141 ->150   -0.12840

Excited State   4:   Triplet-A   1.7277 eV   717.63 nm   f=0.0000
   143 ->145   0.67490
   143 ->147   0.21012

Excited State   5:   Triplet-A   1.9202 eV   645.67 nm   f=0.0000
   142 ->144   0.67077
   142 ->145   -0.23921

3-singlet

Excited State   1:   Singlet-A   0.7500 eV 1653.19 nm   f=0.0002

      143 ->144   0.70688

Excited State   2:   Singlet-A   1.7333 eV   715.31 nm   f=0.0037

      143 ->145   0.70658

Excited State   3:   Singlet-A   1.9531 eV   634.81 nm   f=0.0020

      142 ->144   0.70638

Excited State   4:   Singlet-A   2.2919 eV   540.97 nm   f=0.0009

143 ->146   0.70516

Excited State   5:   Singlet-A   2.3360 eV   530.74 nm   f=0.0458

      141 ->144   -0.21864

      143 ->147   0.66660

4-triplet

Excited State   1:   Triplet-A   0.7819 eV 1585.71 nm   f=0.0000

      155 ->156   0.70682

Excited State   2:   Triplet-A   1.6040 eV   772.95 nm   f=0.0000

      153 ->156   0.33195

      155 ->157   0.12548

      155 ->159   0.59814

Excited State   3:   Triplet-A   1.6057 eV   772.15 nm   f=0.0000

$<S**2>=2.000$

      153 ->156   0.60621

      155 ->159   -0.32593

Excited State   4:   Triplet-A   1.7437 eV   711.04 nm   f=0.0000

      154 ->157   -0.11317

      155 ->157   0.67860

      155 ->159   -0.14323

Excited State   5:   Triplet-A   1.8720 eV   662.29 nm   f=0.0000

154 ->156	0.65718
154 ->157	0.22829
155 ->157	0.10023

4-singlet

Excited State   1:   Singlet-A   0.7836 eV 1582.33 nm   f=0.0002

| 155 ->156 | 0.70654 |

Excited State   2:   Singlet-A   1.7545 eV   706.65 nm   f=0.0040

| 155 ->157 | 0.70545 |

Excited State   3:   Singlet-A   1.9057 eV   650.60 nm   f=0.0021

| 154 ->156 | 0.70536 |

Excited State   4:   Singlet-A   2.2998 eV   539.11 nm   f=0.0490

| 153 ->156 | -0.38684 |
| 155 ->159 | 0.53747 |

Excited State   5:   Singlet-A   2.3324 eV   531.58 nm   f=0.0386

| 153 ->156 | 0.53481 |
| 155 ->159 | 0.37945 |

5-triplet

Excited State   1:   Triplet-A   0.3346 eV 3705.20 nm   f=0.0000

| 149 ->150 | 0.70745 |

Excited State   2:   Triplet-A   1.2143 eV 1021.03 nm   f=0.0000

149 ->151	-0.22453
149 ->152	0.74533
149 ->161	-0.12192

Excited State   3:   Triplet-A   1.2258 eV 1011.44 nm   f=0.0000

| 136 ->150 | -0.11152 |
| 147 ->150 | 0.78008 |

Excited State   4:   Triplet-A   1.2860 eV   964.12 nm   f=0.0000

```
149 ->151          0.66676
149 ->152          0.24438
```

Excited State   5:   Triplet-A   1.4257 eV   869.64 nm   f=0.0000

```
148 ->150          0.68826
148 ->151          -0.16351
```

5-singlet

Excited State   1:   Singlet-A   0.3357 eV 3692.85 nm   f=0.0000

```
149 ->150          0.70686
```

Excited State   2:   Singlet-A   1.2922 eV   959.48 nm   f=0.0040

```
149 ->151          0.70648
```

Excited State   3:   Singlet-A   1.4454 eV   857.77 nm   f=0.0016

```
148 ->150          0.70628
```

Excited State   4:   Singlet-A   1.7749 eV   698.55 nm   f=0.0361

```
147 ->150          -0.41597
149 ->152          0.56958
```

Excited State   5:   Singlet-A   1.8016 eV   688.20 nm   f=0.0317

```
147 ->150          0.56837
149 ->152          0.41539
```

6-triplet

Excited State   1:   Triplet-A   0.8805 eV 1408.13 nm   f=0.0000

```
143 ->144          0.70717
```

Excited State   2:   Triplet-A   1.7412 eV   712.07 nm   f=0.0000

```
141 ->144          0.76914
141 ->150          -0.12416
```

Excited State   3:   Triplet-A   1.7741 eV   698.87 nm   f=0.0000

```
143 ->145          -0.15109
143 ->147          0.74512
```

143 ->148   0.10245

143 ->149   -0.11611

143 ->154   -0.13578

Excited State   4:   Triplet-A   1.9023 eV   651.76 nm   f=0.0000

142 ->145   0.12537

143 ->145   0.67863

143 ->147   0.15634

Excited State   5:   Triplet-A   2.0127 eV   616.01 nm   f=0.0000

142 ->144   0.66698

142 ->145   -0.23231

143 ->145   0.10140

6-singlet

Excited State   1:   Singlet-A   0.8821 eV 1405.56 nm   f=0.0002

143 ->144   0.70660

Excited State   2:   Singlet-A   1.9122 eV   648.38 nm   f=0.0030

143 ->145   0.70566

Excited State   3:   Singlet-A   2.0435 eV   606.72 nm   f=0.0019

142 ->144   0.70541

Excited State   4:   Singlet-A   2.3074 eV   537.34 nm   f=0.0018

143 ->146   0.70628

Excited State   5:   Singlet-A   2.4963 eV   496.68 nm   f=0.0508

141 ->144   0.62382

143 ->147   -0.22054

Absorption and emission of mer-Alq3 at TD-PBE0/6-311+G* level

We have the experimental absorption and emission values of the *mer*-Alq3, to check

the basis set effect, we have used 6-31G* and 6-311+G* basis sets, see Table S2.

Table S2

Calculated absorption and emission wavelengths (nm) for *mer*-Alq3 in S_0 (λ_a) and S_1 (λ_e)[a]

Complex	λ_a	Exp[b]	λ_e	Exp[b]
mer-Alq3	410 (419)	387	523 (536)	515

[a] The λ_a have been calculated at the TD-PBE0/6-31G*//B3LYP/6-31G* and the values in parenthesis are at TD-PBE0/6-311+G*//B3LYP/6-31G*, the λ_e have been calculated at the TD-PBE0/6-31G*//CIS/6-31G* and the values in parenthesis are at TD-PBE0/6-311+G*//CIS/6-31G* level of theories.

[b] Experimental data from reference ref. S38

mer-Alq3 absorption

Excited State　　　Singlet-A　　2.9574 eV　419.23 nm　f=0.0621

117 ->120　　　-0.21298

118 ->120　　　0.13014

118 ->122　　　0.11350

119 ->121　　　0.42951

119 ->122　　　0.42519

mer-Alq3 emission

Excited State　　Singlet-A　　2.3122 eV　536.21 nm　f=0.0398

119 ->120　　　0.63358

119 ->121　　　-0.15585

The excitations attributed from H --> L+1 at the ground states. From the data given in above Tables, we have found that basis set has no significant effect for the *mer*-Alq3 and its derivatives.

Table S3

Calculated absorption and emission wavelengths (nm) of disubstituted derivatives in S_0 (λ_a) at the TD-PBE0/6-31G* and TD-PBE0/6-31+G* level[a]

Complexes	f	Absorption
1	0.1203	416 (423)
2	0.1714	393 (397)
3	0.0877	426 (429)
4	0.0983	439 (447)

[a] The λ_a have been calculated at the TD-PBE0/6-31G*//B3LYP/6-31G* and the values in parenthesis are at TD-PBE0/6-31+G*//B3LYP/6-31G*

Excitations contribution for absorption at TD-PBE0/6-31+G* level

1. Excited State   Singlet-A   2.9325 eV   422.79 nm   f=0.1089

　　153 ->156   -0.25201

　　154 ->156   -0.16482

　　154 ->158   0.10675

　　155 ->157   0.44460

　　155 ->158   -0.37739

2. Excited State   Singlet-A   3.1221 eV   397.11 nm   f=0.1706

　　147 ->150   -0.22737

　　148 ->150   -0.26714

　　149 ->151   0.45668

　　149 ->152   0.31582

3. Excited State   Singlet-A   2.8889 eV   429.17 nm   f=0.0793

　　141 ->144   -0.22921

　　142 ->144   0.12569

　　142 ->146   0.10872

　　143 ->144   0.11458

143 ->145	0.44148
143 ->146	0.40291

4. Excited State   Singlet-A   2.7756 eV   446.70 nm   f=0.0897

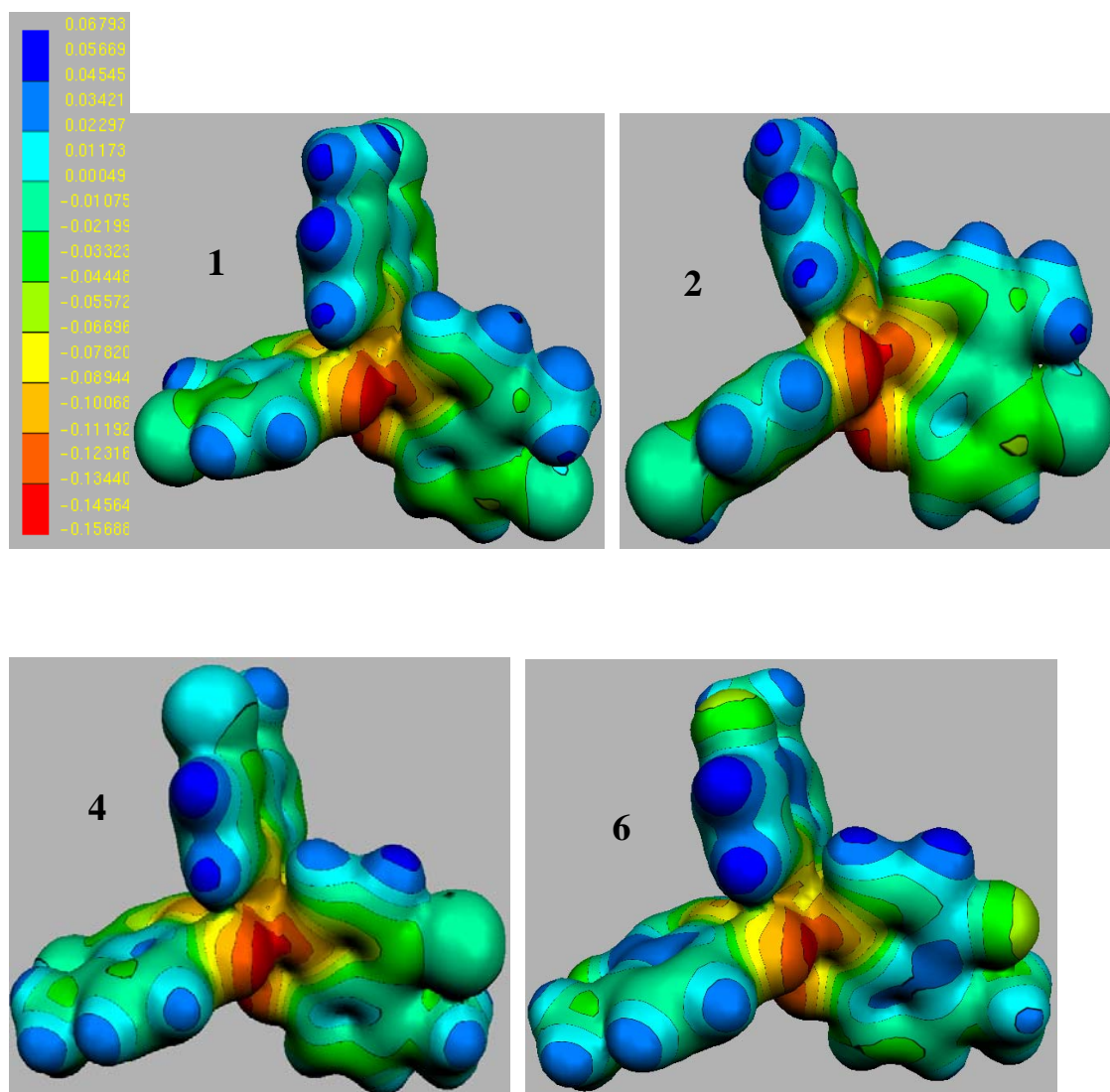| 153 ->156	-0.19743
154 ->156	0.13704
154 ->158	0.11603
155 ->157	0.43297
155 ->158	0.43154

Electrostatic surface potential

Fig. S3. Electrostatic surface potentials for disubstituted derivatives. Regions of higher electron density are shown in red and of lower electron density in blue (values in atomic units)

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