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Supplementary Material

New Perspectives on Photosystem II Reaction Centres

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SI Global Fitting of Luminescence, CPL and MCPL spectra

Attempts were made to simultaneously fit the luminescence, CPL and MCPL spectra with three Gaussian profiles. These correspond to the main luminescence peak at 685 nm, a broader free *Chl-a* component centred near 671 nm and an anomalous, relatively narrow peak at 681 nm. The latter is needed mainly to account for the negative MCPL feature. The main luminescence peak lineshape is not well accounted for as it clearly deviates from Gaussian, but a reasonable account of the overall spectral profiles can be provided, which enables an estimate of the relative areas of the components in the luminescence, CPL and MCPL spectra. These are provided in Fig S1 and Table S1.

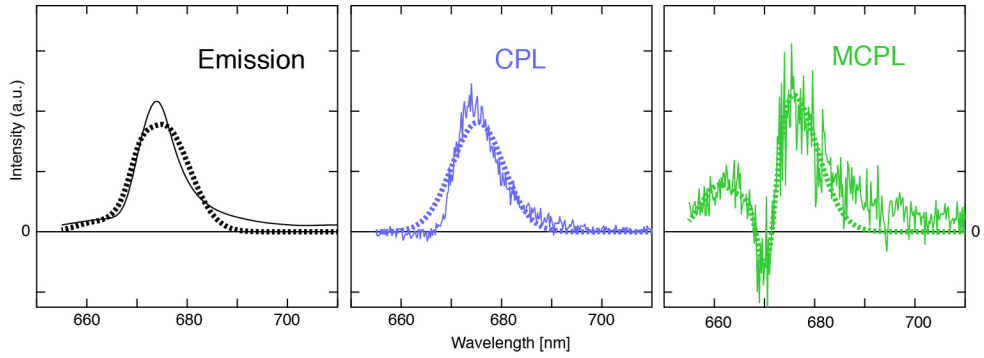

Fig. S1
Luminescence (black) CPL (light blue) and MCPL at 1 T (light green) of RC-6 at 1.8 K, scaled by factors of 1, 1600 and 20000 together with the global fit (thicker dashed curves) *to three Gaussians (See Table S1)*

Table S1

Global fit parameters of Luminescence, CPL and MCPL spectra in Fig. S4 to the Sum of Three Gaussians

Position nm/ (FWHM cm^{-1})	Luminescence	CPL	MCPL
671/(150)	Amplitude=3.7 x 10^{-3} Area=1.8 x 10^{-2} Relative area=0.066	Amplitude=0 ρ_E=0	Amplitude=5.4 x 10^{-6} 1T ρ_E=0.28 x 10^{-3}
681/(100)	Amplitude = 9.8 x 10^{-3} Area=3.1 x 10^{-2} Relative area = 0.115	Amplitude=0 ρ_E=0	Amplitude=-1.2 x 10^{-5} 1T ρ_E=-0.26 x 10^{-3}
685/(190)	Amplitude=3.6 x 10^{-2} Area=0.22 Relative area=0.819	Amplitude=2.5 x 10^{-5} ρ_E=0.69 x 10^{-3}	Amplitude=1.7 x 10^{-5} 1T ρ_E=0.1 x 10^{-3}

SI Exciton Modelling of Absorption and CD spectra of RC-6 and RC-5

Table S2

*RC-5 & RC-6 Site Parameters**

	Site Energy (nm)	FWHM (cm^{-1})
Chl_{D1}	680	140
$Pheo_{D2}$	676	140
$Pheo_{D1}$	669	220
P_{D1}	665.5	220
P_{D2}	665.5	220
Chl_{D2}	669	220
$ChlZ_{D1}$	672	300
$ChlZ_{D2}$	665	300

**The site parameters used for RC5 and RC6 are identical, except that RC5 lacks $ChlZ_{D1}$ at 672 nm. The spectral position and width of $ChlZ_{D1}$ was taken from the subtraction [1] of scaled spectra of RC-6 and RC-5.*

Table S3

PSII RC Coupling matrix[2]

Coupling (cm^{-1})	Chl_{D1}	$Pheo_{D2}$	$Pheo_{D1}$	P_{D1}	P_{D2}	Chl_{D2}	$ChlZ_{D1}$	$ChlZ_{D2}$
Chl_{D1}	0	-2.18	43.51	-27.32	-46.77	3.54	1.67	-0.09
$Pheo_{D2}$	-2.18	0	1.55	12.61	-2.99	41.65	-0.19	-2.57
$Pheo_{D1}$	43.51	1.55	0	-3.96	15.06	-2.37	-2.52	-0.18
P_{D1}	-27.32	12.61	-3.96	0	158	-41.83	0.45	0.58
P_{D2}	-46.77	-2.99	15.06	158	0	-22.04	0.6	0.61
Chl_{D2}	3.54	41.65	-2.37	-41.83	-22.04	0	-0.05	1.8
$ChlZ_{D1}$	1.67	-0.19	-2.52	0.45	0.6	-0.05	0	0.15
$ChlZ_{D2}$	-0.09	-2.57	-0.18	0.58	0.61	1.8	0.15	0

Transition Dipole strengths were taken[2] as 5.47 D for chl-a and 4.25 D for pheo-a.

SI Quantitative Absorption and CD comparison of RC-6 with RC-5

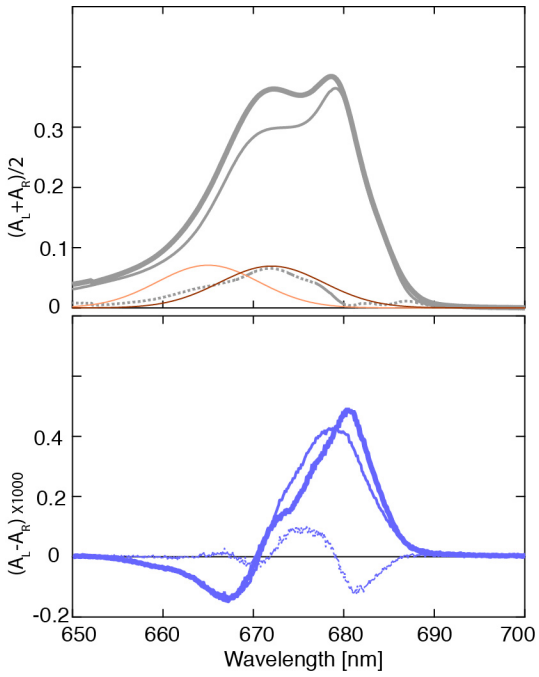

Fig. S2

The top and bottom panels compare the absorption (grey) and CD (blue) spectra of RC-6 (thick) and RC-5 (thin) respectively. Spectra are scaled to two pheo-a molecules per RC, i.e. the same number of reaction centres. Also shown are difference spectra (dotted lines), as well as the modelled absorptions of $ChlZ_{D1}$ (dark brown) and $ChlZ_{D2}$ (light brown).

SI Pigment Distribution of RC excitons

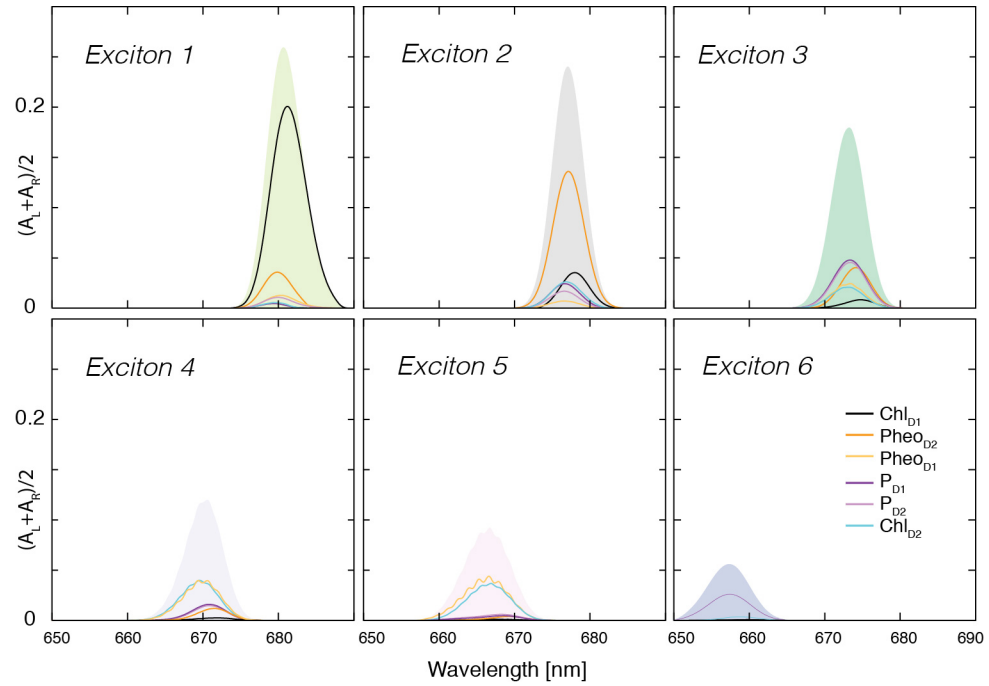

Fig. S3

The pigment distribution of the six excitons of RC-6 and RC-5 in Fig. 6 of the main text are shown in the six panels of the figure. Each filled and coloured profile is one of the excitons. The coloured lines within each profile shows the contribution of each coupled pigment. The colour coding used for pigments in Exciton 6 applies to all excitons.

The pigment distributions shown in Fig. S3 identify which pigments contribute significantly to each exciton. For example, Chl_{D1} dominates Exciton 1 and Exciton 6 is an equal mixture of P_{D1} and P_{D2}. Note that the distribution of each pigment varies and may not have the same lineshape as the exciton itself. This is due to the non-correlated heterogeneity of pigment energies. A less detailed pigment distribution is provided in Fig. 4 of the pioneering 2008 paper[3] by the Renger group.

Supplementary References:

[1] aE. Krausz, N. Cox, S. P. Arskold. Spectral characteristics of PS II reaction centres: as isolated preparations and when integral to PS II core complexes. Photosynthesis Research. **2008**, *98*, 207; bJ. R. Reimers, Z. L. Cai, R. Kobayashi, M. Ratsep, A. Freiberg, E. Krausz. Assignment of the Q-Bands of the Chlorophylls: Coherence Loss via Qx - Qy Mixing. Sci Rep. **2013**, *3*, 2761.

[2] F. Muh, M. Plockinger, T. Renger. Electrostatic Asymmetry in the Reaction Center of Photosystem II. J Phys Chem Lett. **2017**, *8*, 850.

[3] G. Raszewski, B. A. Diner, E. Schlodder, T. Renger. Spectroscopic properties of reaction center pigments in photosystem II core complexes: Revision of the multimer model. Biophysical Journal. **2008**, *95*, 105.