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Incorporation of Zinc(II) Porphyrins in PANI in Its Perigraniline Form Leading to a Conjugated Polymer With the Lowest Band Gap

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Supporting Information

Experiemental Section.

Materials. $TiCl_4$ (Aldrich), 4-iodoaniline (Aldrich), 1,4-diazabicyclo[2.2.2]octane, (DABCO; Aldrich), duroquinone (Aldrich), tetrafluoroquinone (Aldrich), CuI (Aldrich), $PdCl_2(PPh_3)_2$ (Aldrich), PPh_3(Aldrich), $NaBH_4$ (Aldrich) were commercially available and were used as received. Compound **3** and its precursors were prepared according to literature procedures. All reactions were performed in Schlenk-tube flasks under argon atmosphere. All flasks were dried under a flame to eliminate moisture. All solvents were dried with $MgSO_4$ agents.

N,N'-bis(*p*-iodobenzene)tetrafluorobenzoquinone diimine (2a) 4-iodoaniline (4.87 g, 22.2 mmol) and (3.73 g, 33.3 mmol) of DABCO were dissolved in (25 mL) of chlorobenzene while heating to 60°C. Titanium tetrachloride (2.41 mL, 22.2 mmol) were then added dropwise, followed by the addition of p-Fluoranil (2.00 g, 11.1 mmol) and rinsing the powder addition funnel with 20 mL of chlorobenzene. The solution was stirred at 60^0C for a 5 hrs period. The precipitate was filtered, washed with hot chlorobenzene (2 x 40 mL). The solution was evaporated. The resulting solid was dissolved in $CHCl_3$, washed three times with water, dried with $MgSO_4$, and filtered. The $CHCl_3$ was completely evaporated leaving product and side products. The product was purified on an alumina column with $CHCl_3$ as the solvent to give compound **2a**. Yield: 2.45 g (38%). IR (KBr)/cm^{-1} ν: 1630 (C=N). ^{1}H NMR δ (400 MHz, $CDCl_3$): 7.68 (4 H, dd, *J*=8.4 Hz, 6.0, C-H aro), 6.67 (4 H, m, CH aro.), ppm; λ_{max}(2-MeTHF)/nm (ε/$dm^3.mol^{-1}.cm^{-1}$) 260 (28000), 295 (48900), 515 (13700)); m/z (EI): 582 (M+).

N,N'-bis(*p*-iodobenzene)tetrafluorobenzoquinone diamine (5a) was formed *in situ* in the previous reaction as a bi-product and separated from its oxidized form by the alumina column chromatography mentioned above leading to the white product **5a** (0.77 g, 12%); IR (KBr)/cm^{-1} ν : 3416 (N-H). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J*=8.8, 4H, C-H aro), 6.61 (d, *J*=8.6, 4H, C-H aro), 5.46 (s, 2H, N-H) ppm; m/z (EI): 584(M+).

N,N'-bis(*p*-iodobenzene)tetramethylbenzoquinone diimine (2b) 4-iodoaniline (8.00 g, 36.5 mmol) and (6.45 g, 54.9 mmol) of DABCO were dissolved in 200 mL of chlorobenzene while heating at 60°C. Titanium tetrachloride (4.00 mL, 36.5 mmol) was added dropwise, followed by the addition of tetramethylbenzoquinone (3.00 g, 18.3 mmol). The solution was stirred at 60^{0}C for 5 hrs. The precipitate was filtered off, and washed with hot chlorobenzene (2 x 60 mL). The solution was evaporated and the resulting solid was dissolved in $CHCl_3$, washed three times with water, dried with $MgSO_4$, and filtered. The $CHCl_3$ was completely evaporated. The resulting product was purified on an alumina column with $CHCl_3$ as the solvent to give compound **2b**. Yield: (8.21 g, 79%). IR (KBr)/cm^{-1} ν: 1632 (C=N).^{1}H NMR δ (400 MHz $CDCl_3$): 7.60 (4H, d, *J*=8.6, C-H aro), 6.57 (4H, d, CH aro), 2.19 (6H, s br) 1.33 (6H, s br) ppm; λ_{max}(2MeTHF)/nm (ε/dm^3.mol^{-1}.cm^{-1}) 250 (18000), 305 (30000), 433 (7900)); m/z (EI): 566 (M+).

N,N'-bis(*p*-iodobenzene)tetramethylbenzoquinone diamine (5b) An argon degassed solution of $NaBH_4$ (0.450 g, 1.19 mmol, 5 equivs.) in absolute ethanol (50 mL) was added dropwise, with a funnel to an argon degassed solution of N,N'-bis(*p*-iodobenzene)-tetramethylbenzoquinone diimine (**2b**) (1.35 g, 2.38 mmol) in $CHCl_3$ (50 mL) at room temperature. The resulting mixture was stirred overnight at room temperature under argon flux. Water (5 mL) was added dropwise to quench the excess of $NaBH_4$, and the solution was evaporated to dryness. The solid was dissolved in $CHCl_3$ and washed three times with water, dried with $MgSO_4$, and filtered. $CHCl_3$ was completely evaporated and the product was purified on a silica column with $CHCl_3$/hexanes (1/2) as the solvent. The solvent was evaporated to dryness leaving the white product **5b** (1.224 g, 90%); IR (KBr)/cm^{-1} ν: 3387 (N-H). ^{1}H NMR δ (400 MHz $CDCl_3$): 7.41 (4H, d, *J*=8.6, C-H aro), 6.26 (4H, d, *J*=8.6 CH aro.), 5.23 (2H, s, N-H), 2.14 (12H, s, CH_3) ppm; λ_{max}(2MeTHF)/nm (ε/dm^3.mol^{-1}.cm^{-1}) 260 (35600), 288 (21600); m/z (EI): 568 (M+).

Poly{N,N'-[5,15-bis(3,4,5-tri(n-hexadecanyl)benzene)-10,20-di(ethynyl)porphinato-zinc(II)]tetramethylbenzoquinone diimine} (4b): **3** (150 mg, 0.080 mmol), was added to a degassed solution of $PdCl_2(PPh_3)_2$ (10% eq, 0.008 mmol), PPh_3 (20% eq, 0.016 mmol), CuI (10% eq, 0.008 mmol), and **5b** (42 mg, 0.08 mmol) in 60 mL of toluene and 30 mL of diisopropylamine while bubbling with argon for 20 min at room temperature. The resulting mixture was stirred at room temperature overnight. The solution was evaporated to dryness. The solid was dissolved in CH_2Cl_2, washed three times with water, dried with $MgSO_4$, and filtered. The CH_2Cl_2 was completely evaporated. The solid was washed by acetone to remove a small amount of unknown green product leaving the main green product **(4b)**. Yield: (0.151g, 83%). Chem. anal.: Theor. for $[C_{154}H_{232}N_6O_6Zn]_n$: C, 75.29; H, 9.56; N, 3.42; O, 3.91, Found: C, 75.22; H, 9.54; N, 3.29. O, 4.14 $[C_{154}H_{232}N_6O_6Zn]_n$; IR (KBr)/cm^{-1} ν: 3388 (N-H), 2185 (C≡C); ^{1}H NMR δ (400 MHz, $CDCl_3$) 9.85 (br, *β* porph), 9.06 (br, *β* porph), 8.04

(br, aro), 7.83 (br, aro), 7.55 (br, aro), 7.40 (br, aro porph), 7.02 (br, aro quinone), 6.64 (br, aro quinone), 6.22 (br, aro quinone), 4.18 (br, α ether porph), 2.28 (s, CH3 quinone), 2.16 – 0.84 (br, aliphatic); λ_{max}(2MeTHF)/nm 464 nm (ε/dm^3.mol^{-1}.cm^{-1} 133000), 493 (63100), 586 (7380), 682 (26700), 747 (29000)); GPC (THF) : M_n = 10280; M_w = 13780; PD 1.34 .

Poly{N,N'-[5,15-bis(3,4,5-tri(n-hexadecanyl)benzene)-10,20-di(ethynyl)porphinato-zinc(II)]fluorobenzoquinone diimine} (4a) 3 (75 mg, 0.037 mmol), was added to a degassed solution of $PdCl_2(PPh_3)_2$ (10% eq, 0.004 mmol), PPh_3 (20% eq, 0.008mmol), CuI (10% eq, 0.004 mmol), and **2a** (22 mg, 0.037 mmol) in 60 mL of toluene and 30 mL of diisopropylamine while bubbling with argon for 20 min at room temperature. The resulting mixture was stirred at room temperature overnight. The solution was evaporated to dryness. The solid was dissolved in CH_2Cl_2, washed three times with water, dried with $MgSO_4$, and filtered. The CH_2Cl_2 was completely evaporated. The solid was washed with acetone to remove a small amount of unknown green product leaving the main green product (**4a**). Yield: (69 mg, 76%). Chem. anal.: Theor. for $[C_{154}H_{232}N_6O_6Zn]_n$: C, 72.92; H, 8.93; N, 3.40; O, 3.89, Found: C, 73.20; H, 8.92; N, 3.29. O, 3.85; IR (KBr)/cm^{-1} ν: 2183, 2125 (C≡C). ^{1}H NMR δ (400 MHz, $CDCl_3$) 9.87 (br, β porph), 9.10 (br, β porph), 7.76 (br, aro quinone), 7.41 (br, aro porph), 7.18–6.32 (m, br, aro quinine), 4.21 (br, CH2 α ether porph), 2.34–0.32 (m, br, H aliphatic) ppm; λ_{max}(2MeTHF)/nm (ε/dm^3.mol^{-1}.cm^{-1}) 463 nm (181400), 490 (101300), 583 (12300), 675 (30200), 735 (45800)); M_n = 14700; M_w = 20460; PD 1.39.

Alternative route for **4a**: **3** (100 mg, 0.050mmol), was added to a degassed solution of $PdCl_2(PPh_3)_2$ (10% eq, 0,005 mmol), PPh_3 (20% eq, 0,010 mmol), CuI (10% eq, 0.005 mmol), and N,N'-bis(*para*-ethynylphenyl)tetrafluorobenzoquinone diamine (**2b**) (30 mg, 0.05 mmol) in 60 mL of toluene and 30 mL of diisopropylamine while bubbling with argon for 20 min at room temperature. The resulting mixture was stirred at room temperature overnight. The solution was evaporated to dryness. The solid was dissolved in CH_2Cl_2, washed three times with water, dried with $MgSO_4$, and filtered. The CH_2Cl_2 was completely evaporated. The solid was washed with acetone to remove a small amount of unknown green product leaving the main green product (**4a**). Yield: (97 mg, 81%). IR (KBr)/cm^{-1} ν: 2183, 2125 (C≡C). ^{1}H NMR δ (400 MHz, $CDCl_3$) 9.87 (br, β porph), 9.10 (br, β porph), 7.76 (br, aro quinone), 7.41 (br, aro porph), 7.18–6.32 (m, br, aro quinone), 4.21 (br, CH2 α ether porph), 2.34–0.32 (m, br, H aliphatic) ppm; λ_{max}(2MeTHF)/nm (ε/dm^3.mol^{-1}.cm^{-1}) 463 (181400), 490 (101300), 583 (12300), 675 (30200), 735 (45800)); M_n = 18050; M_w = 24140; PD 1.34.

Intrumentation. UV-visible spectra were recorded on a Hewlett-Packard diode array model 8452A and the emission spectra were obtained using a double monochromator Fluorolog 2 instrument from Spex. The emission lifetimes were measured using a TimeMaster Model TM-3/2003 apparatus from PTI. The source was nitrogen laser with high-resolution dye laser (fwhm ~1500 ns) and fluorescence lifetimes were obtained from deconvolution or distribution lifetimes analysis. Time-resolved spectra were obtained on the same PTI instrument as for the measurements of the fluorescence lifetimes.

Quantum yields. Measurements of quantum yields were performed in 2MeTHF at 298K. Three different measurements (*i.e.* different solutions) were prepared for each photophysical datum (quantum yields and lifetimes). For 298K measurements samples were prepared under inert atmosphere (in a glove box, P_{O_2} < 25 ppm). The sample and standard concentrations were adjusted to obtain an absorbance of 0.05 or less. This absorbance was adjusted to be the same as much as possible for the standard and the sample for a measurement. Each absorbance value was measured five times for better accuracy in the measurements of the quantum yields. ^{b}Reference used is rhodamine 6G (Φ_F = 0.95; R.F. Kubin and A.N. Fletcher *J. Lumin.* 1982, **27**, 455).

X-ray structure determination. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC(1) program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection. The data were corrected for absorption by empirical methods based on psi scans and reduced with the NRCVAX(2) programs. They were solved using SHELXS-97(3) and refined by full-matrix least squares on F^2 with SHELXL-97(4). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model.

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X-ray structure for 5a. The crystals were grown by slow evaporation of a $CHCl_3$ solution at room temperature. One single crystal of 0.15 X 0.30 X 0.55 mm^3 was mounted using a glass fiber at 293(2) K on the goniometer.

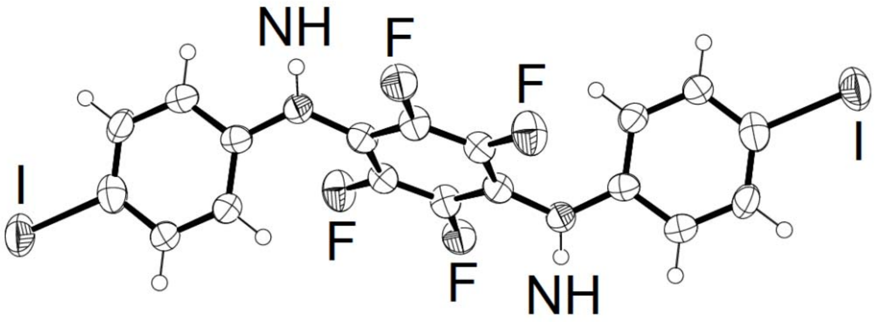

Figure S1. ORTEP representation of **5a**. The thermal ellipsoids are shown at 30% probability.

Table S1. Crystal data and structure refinement for **5a**.

Empirical formula	C18 H10 F4 I2 N2	
Formula weight	584.08	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnaa	
Unit cell dimensions	a = 5.793(2) Å	α= 90°.
	b = 8.312(5) Å	β= 90°.
	c = 36.680(13) Å	γ = 90°.
Volume	1766.0(14) Å^3	
Z	4	
Density (calculated)	2.197 Mg/m^3	
Absorption coefficient	3.606 mm^{-1}	
F(000)	1096	
Crystal size	0.55 x 0.30 x 0.15 mm^3	
Theta range for data collection	1.11 to 25.56°.	
Index ranges	0<=h<=7, 0<=k<=10, 0<=l<=44	
Reflections collected	1654	
Independent reflections	1654 [R(int) = 0.0000]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.6138 and 0.2417	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1654 / 0 / 119	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1172	
R indices (all data)	R1 = 0.1149, wR2 = 0.1330	
Extinction coefficient	0.0016(3)	
Largest diff. peak and hole	0.748 and -0.614 e.Å^{-3}	

X-ray structure for 5a. The crystals were grown by slow evaporation of THF at room temperature**.** One single crystal of 0.03 X 0.30 X 0.35 mm^3 was mounted using a glass fiber at 193(2) K on the goniometer.

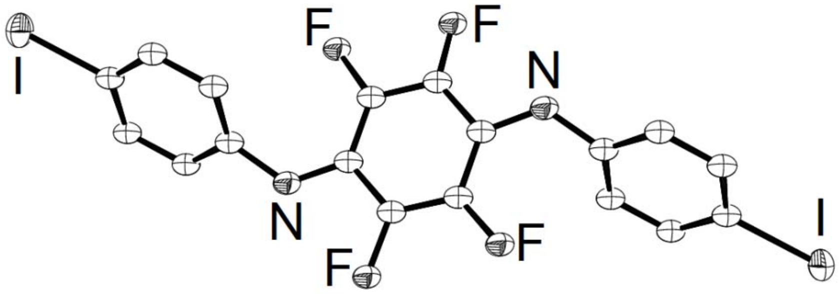

Figure S2. ORTEP representation of **2a**. The thermal ellipsoids are shown at 30% probability.

Table S2. Crystal data and structure refinement for **2a**.

Empirical formula	C18 H8 F4 I2 N2	
Formula weight	582.06	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna21	
Unit cell dimensions	a = 5.887(2) Å	α = 90°.
	b = 7.940(2) Å	β = 90°.
	c = 36.911(11) Å	γ = 90°.
Volume	1725.2(10) Å^3	
Z	4	
Density (calculated)	2.241 Mg/m^3	
Absorption coefficient	3.690 mm^{-1}	
F(000)	1088	
Crystal size	0.35 x 0.30 x 0.03 mm^3	
Theta range for data collection	2.62 to 25.55°.	
Index ranges	0<=h<=7, 0<=k<=9, 0<=l<=44	
Reflections collected	1589	
Independent reflections	1589 [R(int) = 0.0000]	
Completeness to theta = 25.50°	97.2 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.8973 and 0.3583	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1589 / 4 / 69	
Goodness-of-fit on F^2	0.886	
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1179	
R indices (all data)	R1 = 0.1687, wR2 = 0.1492	
Absolute structure parameter	0.0(5)	
Extinction coefficient	0.0009(2)	
Largest diff. peak and hole	1.726 and -1.267 e.Å^{-3}	

X-ray structure for 5b. The crystals were grown by slow evaporation of a $CHCl_3$ solution at room temperature**.** One single crystal of 0.20 X 0.30 X 0.40 mm^3 was mounted using a glass fiber at 293(2) K on the goniometer.

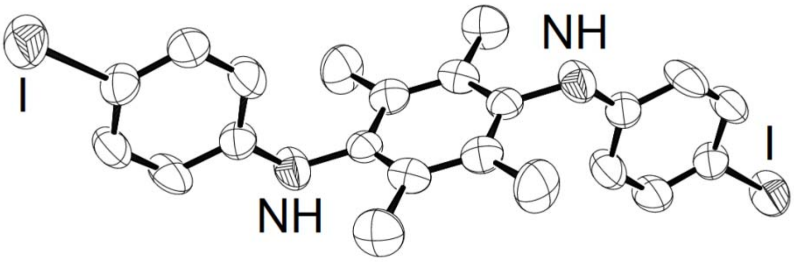

Figure S3. ORTEP representation of **5b**. The thermal ellipsoids are shown at 50% probability.

Table S3. Crystal data and structure refinement for **5b**.

Empirical formula	C22 H22 I2 N2	
Formula weight	568.22	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	p-1	
Unit cell dimensions	a = 8.632(2) Å	α = 72.46(4)°.
	b = 10.136(5) Å	β = 78.12(3)°.
	c = 13.097(6) Å	γ = 79.22(4)°.
Volume	1059.5(7) $Å^3$	
Z	2	
Density (calculated)	1.781 Mg/m^3	
Absorption coefficient	2.976 mm^{-1}	
F(000)	548	
Crystal size	0.40 x 0.30 x 0.20 mm^3	
Theta range for data collection	1.65 to 25.54°.	
Index ranges	-10<=h<=10, 0<=k<=12, -14<=l<=15	
Reflections collected	3953	
Independent reflections	3953 [R(int) = 0.0000]	
Completeness to theta = 25.50°	99.9 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.5875 and 0.3823	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3953 / 0 / 236	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1439	
R indices (all data)	R1 = 0.1141, wR2 = 0.1639	
Extinction coefficient	0.0026(10)	
Largest diff. peak and hole	1.048 and -1.108 e.$Å^{-3}$	

DFT Computations. Calculations were performed with Gaussian 09(1) at the Université de Sherbrooke with Mammouth super computer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT(2-5) and TD-DFT(6-8) were calculated with the B3LYP(9-11) method and 3-21G*(12-17) basis sets. The calculated absorption spectra and related MO contributions were obtained from the TD-DFT/Singlets output file and gausssum2.1.(18)

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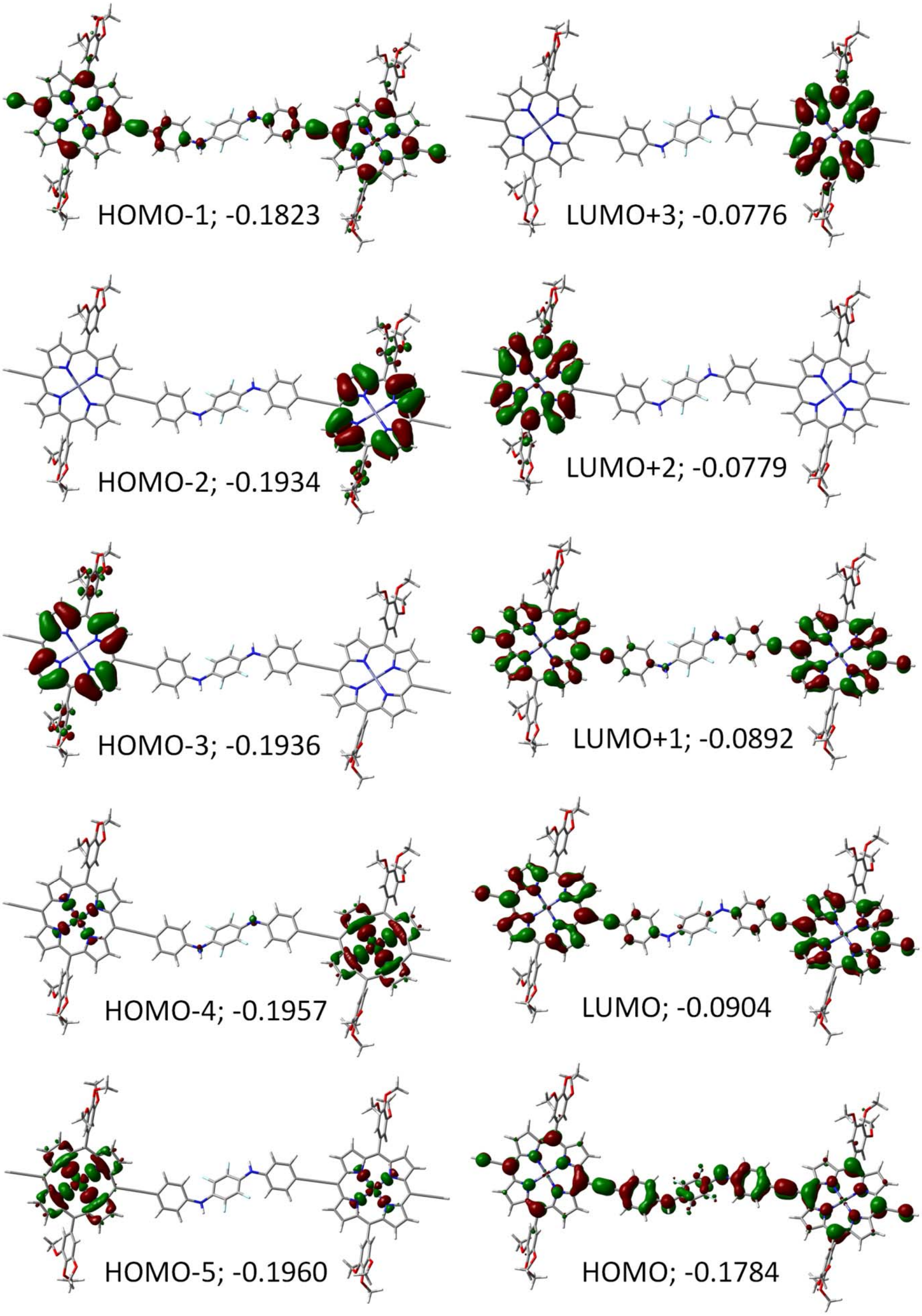

Figure S4. MO representation of the frontier MOs for the reduced form (1,4-diaminobenzene) of the model for polymer **4**. The MO energies are in a.u.

Table S4. TDDFT calculated positions and the oscillator strengths (f) of the 20 first electronic transitions of the reduced form (1,4-diaminobenzene) of the model for polymer **4**.

No.	ν (cm^{-1})	λ (nm)	f	Major contributions (%)
1	16660	600	0.315	H-5→L+1 (26), H-4→LUMO (31), HOMO→LUMO (19)
2	16730	598	0.002	H-5→LUMO (40), H-4→L+1 (35)
3	17390	575	1.180	H-5→L+1 (11), H-4→LUMO (12), HOMO→LUMO (56)
4	17910	558	0.001	H-1→LUMO (15), HOMO→L+1 (54)
5	18010	555	0.002	H-3→LUMO (21), H-3→L+1 (17), H-1→L+2 (24), HOMO→L+2 (31)
6	18020	555	0.002	H-2→LUMO (19), H-2→L+1 (20), H-1→L+3 (22), HOMO→L+3 (33)
7	18860	530	0.000	H-1→LUMO (63), HOMO→L+1 (31)
8	18990	526	0.001	H-5→L+3 (14), H-4→L+3 (77)
9	19000	526	0.000	H-5→L+2 (78), H-4→L+2 (13)
10	19030	526	0.001	H-1→L+1 (70), HOMO→LUMO (19)
11	21410	467	0.011	H-1→L+2 (37), HOMO→L+2 (58)
12	21490	465	0.014	H-1→L+3 (40), HOMO→L+3 (54)
13	21790	459	1.032	H-6→LUMO (59)
14	21850	458	0.006	H-2→LUMO (54), H-2→L+1 (45)
15	21910	456	0.002	H-3→LUMO (47), H-3→L+1 (52)
16	22290	449	0.009	H-6→L+1 (19), H-5→LUMO (22), H-4→L+1 (38)
17	22450	445	0.068	H-5→L+1 (42), H-4→LUMO (35)
18	22610	442	0.011	H-6→L+1 (51), H-5→LUMO (19)
19	23070	433	0.143	H-7→LUMO (31), H-7→L+1 (30), H-1→L+3 (10)
20	23200	431	0.141	H-9→LUMO (32), H-9→L+1 (22), H-8→LUMO (13), H-8→L+1 (10)

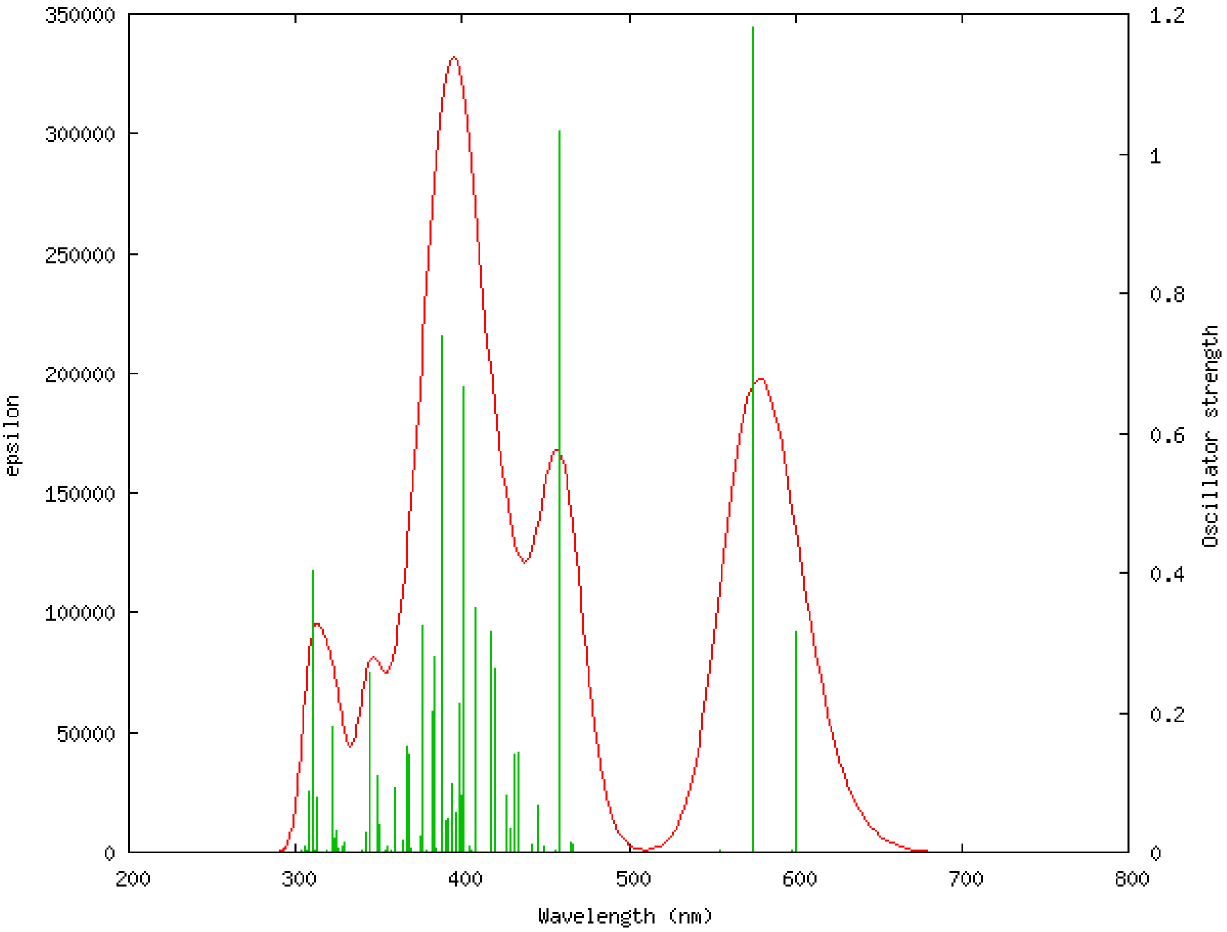

Figure S5. Graph representing the calculated oscillator strength (f) and epsilon for the 100 first electronic transitions of the reduced form (1,4-diaminobenzene) of the model for polymer **4**.

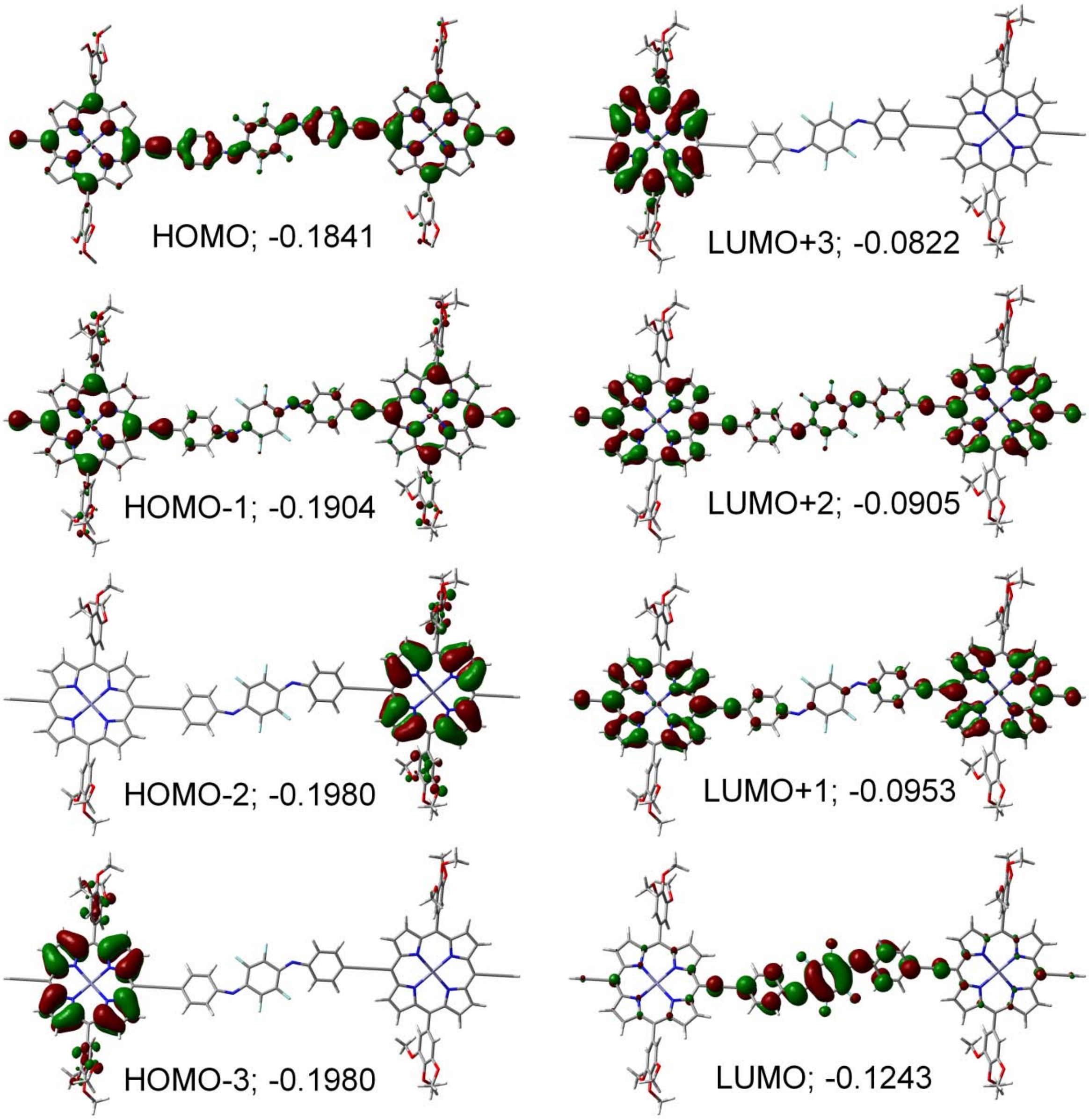

Figure S6. MO representation of the frontier MOs for the oxidized form (benzoquinone diimine) of the model for polymer **4**. The MO energies are in a.u **.**

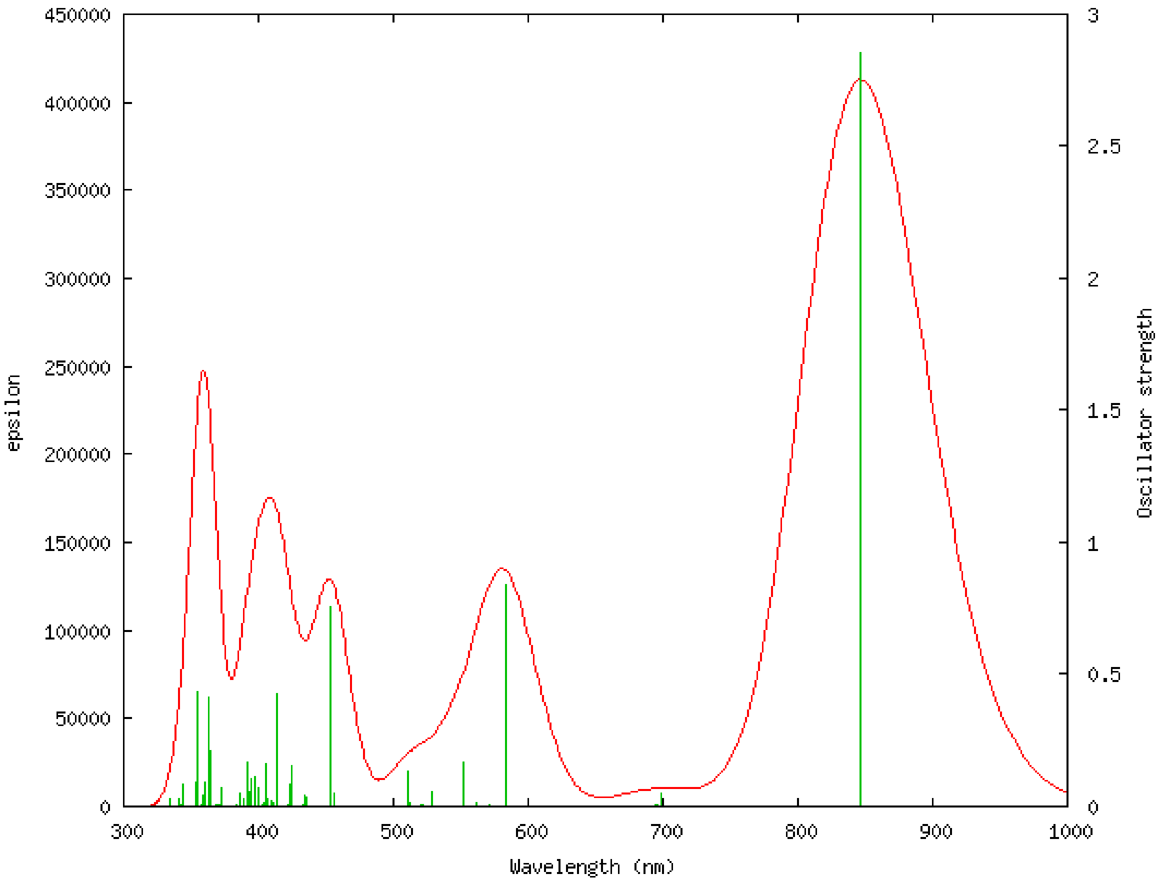

Figure S7. Graph representing the calculated oscillator strength (f) and epsilon for the 100 first electronic transitions of the oxidized form (benzoquinone diimine) of the model for polymer **4.**

Table S5. TDDFT calculated positions and the oscillator strengths (f) of the 20 first electronic transitions of the oxidized form (benzoquinone diimine) of the model for polymer **4**.

No.	ν (cm^{-1})	λ (nm)	f	Major contributions (%)
1	11808	847	2.851	HOMO→LUMO (99)
2	13461	743	0.003	H-1→LUMO (94)
3	14320	698	0.050	H-4→LUMO (88)
4	14375	696	0.008	H-2→LUMO (97)
5	14388	695	0.008	H-3→LUMO (96)
6	14397	695	0.002	H-5→LUMO (83)
7	17122	584	0.839	H-6→LUMO (73), HOMO→L+2 (11)
8	17521	571	0.009	H-9→LUMO (11), H-5→L+2 (11), H-4→L+1 (14), HOMO→L+1 (37)
9	17607	568	0.002	H-7→LUMO (93)
10	17638	567	0.003	H-8→LUMO (93)
11	17693	565	0.001	H-10→LUMO (11), H-6→LUMO (14), H-5→L+1 (23), H-4→L+2 (20)
12	17788	562	0.012	H-9→LUMO (80)
13	18110	552	0.045	H-10→LUMO (11), H-5→L+1 (10), H-5→L+2 (17), H-4→L+1 (16), HOMO→L+1 (28)
14	18124	552	0.169	H-10→LUMO (37), H-5→L+1 (10), H-4→L+1 (10), H-4→L+2 (13)
15	18465	542	0.003	H-3→L+1 (24), H-3→L+2 (13), H-1→L+3 (18), HOMO→L+3 (32)
16	18477	541	0.003	H-2→L+1 (23), H-2→L+2 (14), H-1→L+4 (18), HOMO→L+4 (32)
17	18909	529	0.057	H-14→LUMO (25), H-10→LUMO (28), HOMO→L+2 (14)
18	19145	522	0.008	H-12→LUMO (15), H-11→LUMO (71)
19	19166	522	0.000	H-12→LUMO (19), H-5→L+4 (18), H-4→L+4 (49)
20	19170	522	0.000	H-12→LUMO (41), H-5→L+3 (22), H-4→L+4 (11)

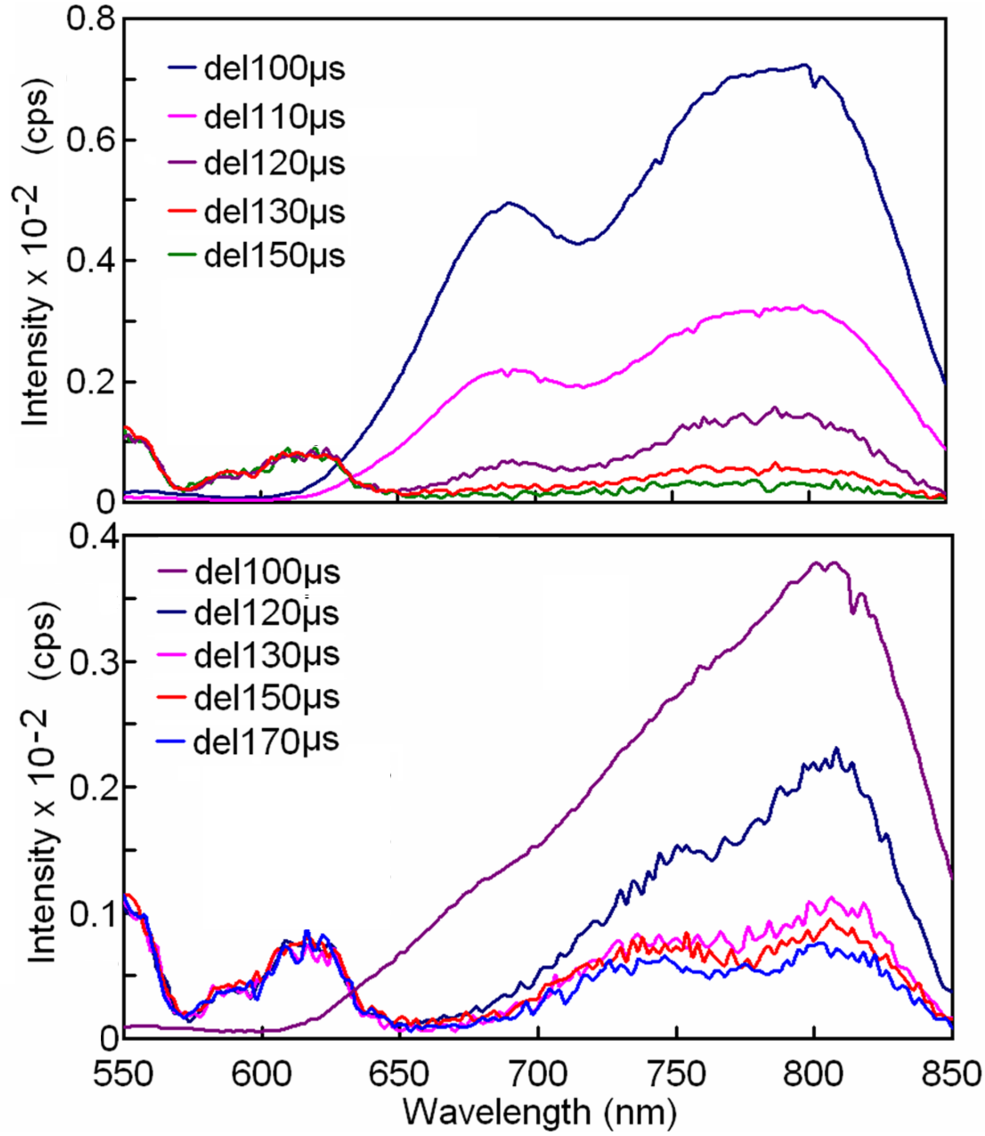

Figure S8. Time-resolved emission spectra of **4** (up) and **6** (down) in 2MeTHF at 298 K. The spectral intensities are uncorrected for instrument response. The delay times are indicated in the frames; λ_{exc} = 480 nm.