Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Phosphorescent Emission from Spatial Stacks of Phenanthrene Units in Oligo(9,10-phenanthrene)s

T. Kawata, M. Sonobe, D. Morikawa, Y. Kitazawa, Y. Nomura, M. Uchiyama, and M. Kimura*

General

NMR spectra were recorded on a Bruker AVANCE NEO400 OneBay NMR spectrometer at 400.13 and 100.62 MHz for ^{1}H and ^{13}C in $CDCl_3$ or MeOD solutions. Chemical shifts are reported relative to internal TMS. UV-Vis, fluorescence, and phosphorescence spectra were measured on a SHIMAZU UV2600 and a JASCO FP-750. High resolution time-of-flight mass spectra with atmospheric pressure chemical ionization (HR-APCI-TOF-Ms) were obtained on a Bruker Daltonics micrOTOFII. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-Ms) was performed on a Bruker microflexLT using dithranol as a matrix. DFT and TD-DFT calculations were performed using the Coulomb-attenuating B3LYP (CAM-B3LYP)/6-31+G(d) and CAM-B3LYP/6-311+G(d,p) basis set as implemented in the Gaussian 16 software suit. All chemicals were purchased from commercial supplies used without further purification. Column chromatography was performed with silica gel (Wakogel C-200) or activated alumina (Wako, 200 mesh). Recycling preparative gel permeation chromatography was carried out by a JAI recycling preparative HPLC using $CHCl_3$ as an eluent. Gel permeation chromatography was performed at 303 K on a Shodex GPC KF-804L column with a JASCO UV-1575 UV detector and a JASCO RI-930 RI detector using THF as an eluent at a flow rate of 1 mL/min. Analytical thin layer chromatography was performed with commercial Merck plates coated with silica gel 60 F254 or aluminum oxide 60 F254.

Synthesis

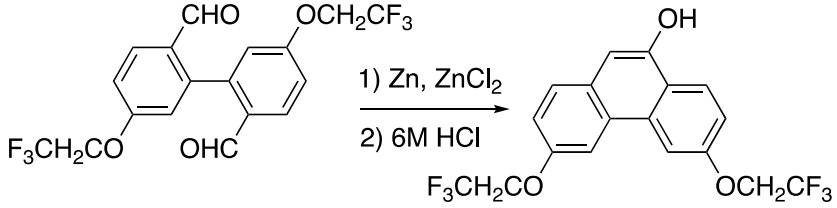
2-Bromo-4-trifluoroethoxybenzaldehyde (3)

A solution of 2-bromo-4-fluorobenzaldehyde (1.0 g, 4.9 mmol) and trifluoroethanol (0.54 g, 5.4 mmol) were stirred in DMF (5 mL) under Ar atmosphere. Dry K_2CO_3 (2.7 g, 10.8 mmol) was added to the reaction mixture and the reaction mixture was heated to 70°C for overnight. A reaction mixture was extracted with CH_2Cl_2. After the evaporation of solvents, the crude product was purified by silica column chromatography (CH_2Cl_2/hexane = 2:1) and recycling preparative HPLC ($CHCl_3$) to obtain **3**. Yield 79%. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 10.25(1H, s, -C*H*O), 7.93 (1H, d, *J* = 8.8Hz, Ar*H*), 7.21 (1H, s, Ar*H*), 7.00 (1H, d, *J* = 8.8Hz, Ar*H*), 4.43 (2H, m, -CH_2-); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ (ppm) = 190.33, 161.62, 131.63, 122.74 (q, *J* = 287.1 Hz), 119.58, 114.42, 65.69(q, *J* = 36.6 Hz); HR-APCI-TOF Ms: *m*/*z* 282.9556 (calcd *m*/*z* 282.9576 for $C_9H_6BrF_3O_2$ [M+H]).

5,5'-Bis(trifluoroethoxy)biphenyl-2,2'-dicarboxaldehyde (4)

A solution of **3** (0.30 g, 1.1 mmol), bis(pinacolato)diboron (0.16 g, 0.64 mmol) and K_3PO_4 (0.68 g, 3.2 mmol) were stirred in DMF (3.9 mL) under Ar atmosphere. $PdCl_2(dppf)_2$ · CH_2Cl_2 (26 mg, 0.032 mmol) was added to the reaction mixture and the reaction mixture was heated to 80°C for 3.5 h. A reaction mixture was extracted with CH_2Cl_2. After the evaporation of solvents, the crude product was purified by flash silica column chromatography (hexane/EtOAc = 3:1) to obtain **4**. Yield 84%. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 9.68 (2H, s, -C*H*O), 8.03 (2H, d, *J* = 8.4Hz, Ar*H*), 7.15 (2H, d, *J* = 8.4Hz, Ar*H*), 6.91 (2H, s, Ar*H*), 4.78 (4H, m, -CH_2-); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ (ppm) = 189.21, 160.66, 143.01, 131.44, 129.45, 123.74 (q, *J* = 287.3 Hz), 117.18, 114.93, 65.57 (q, *J* = 36.4 Hz), 24.80; HR-APCI-TOF Ms: *m*/*z* 407.0759 (calcd *m*/*z* 407.0713 for $C_{18}H_{12}F_6O_4$ [M+H]).

3,6-Bis(trifluoroethoxy)phenanthrene-9-ol



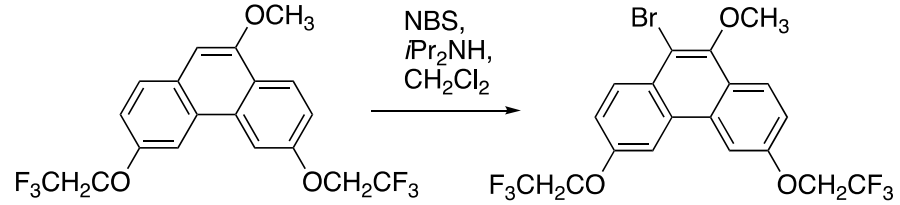
A solution of **4** (0.54 g, 1.3 mmol), zinc (0.22 g, 3.3 mmol) and zinc chloride (0.18 g, 1.3

mmol) were stirred in DMF (1.62 mL) under Ar atmosphere. The reaction mixture was heated to 70°C for 4 h. After cooling by ice bath, DMF (15 mL) and 6 M HCl (10.8 mL) were added to the reaction mixture. The reaction mixture was heated to 110°C for 2 h. The reaction mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Mg_2SO_4 and the solvent was evaporated. The crude product was purified by silica column chromatography (hexane/EtOAc = 3:1) to get 3,6-Bis(trifluoroethoxy)phenanthrene-9-ol. Yield 67%. ^{1}H NMR (methanol-d_4, 400.13 MHz): δ (ppm) = 8.25 (1H, d, J = 9.1Hz, Ar*H*), 8.05 (1H, s, Ar*H*), 8.01 (1H, s, Ar*H*), 7.58 (1H, d, J = 8.8Hz, Ar*H*), 7.27 (1H, d, J = 8.8Hz, Ar*H*), 7.18 (1H, d, J = 8.8Hz, Ar*H*), 6.87 (1H, s, Ar*H*), 4.71 (4H, m, -C*H*$_2$-); ^{13}C NMR (methanol-d_4, 100.61 MHz): δ (ppm) = 156.41, 154.07, 149.91, 132.31, 129.52, 127.81, 126.26, 124.45, 122.65 (q, J = 287.1 Hz), 117.11, 116.00, 105.52, 105.14, 102.96, 65.49 (q, J = 36.3 Hz); HR-APCI-TOF Ms: m/z 391.0742 (calcd m/z 391.0763 for $C_{18}H_{12}F_6O_3$ [M+H]).

3,6-Bis(trifluoroethoxy)-9-methoxyphenanthrene (7)

A solution of 3,6-bis(trifluoroethoxy)phenanthren-9-ol (0.19 g, 0.48 mmol) and K_2CO_3 (0.20 g, 1.5 mmol) were stirred in DMF (4.8 mL) under Ar atmosphere. DMF solution (4.8 mL) of CH_3I (55 mg, 0.39 mmol) was added dropwise to the reaction mixture. The reaction mixture was stirred for overnight at room temperature under Ar atmosphere. The reaction mixture was extracted with CH_2Cl_2. After the evaporation of solvents, the crude product was purified by silica column chromatography (CH_2Cl_2) and recycling preparative HPLC ($CHCl_3$) to obtain **7**. Yield 58%. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 8.29 (1H, d, J = 8.8Hz, Ar*H*), 7.84 (2H, d, J = 11.6Hz, Ar*H*), 7.68 (1H, d, J = 8.8Hz, Ar*H*), 7.23 (2H, m, Ar*H*), 4.52 (4H, m, -C*H*$_2$-) 4.03 (3H, s, -OC*H*$_3$). HR-APCI-TOF Ms: m/z 405.0707 (calcd m/z 405.0921 for $C_{19}H_{14}F_6O_3$ [M+H]).

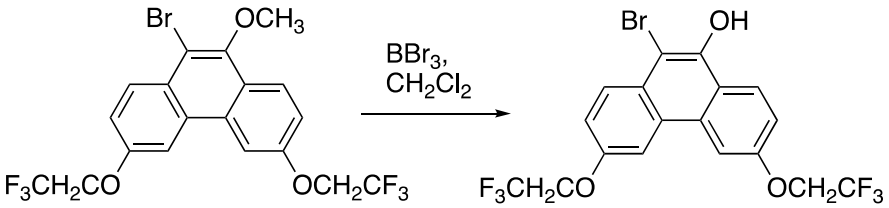
3,6-Bis(trifluoroethoxy)-10-bromo-9-methoxyphenanthrene



A solution of **7** (0.20 g, 0.49 mmol) and *i*-Pr_2NH (5 mg, 49 μmol) were stirred in CH_2Cl_2 under Ar atmosphere. NBS (0.13 g, 0.74 mmol) was added to the reaction mixture and

the reaction mixture was stirred at room temperature for 3.5 h. A reaction mixture was quenched by the addition of water and extracted with CH_2Cl_2. The combined organic phases were dried over Mg_2SO_4 and the solvent was evaporated. The crude product was purified by flash silica column chromatography (hexane/EtOAc = 5:1) and recycling preparative HPLC ($CHCl_3$) to get 3,6-bis(trifluoroethoxy)-10-bromo-9-methoxyphenanthrene. Yield 64%. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 8.10 (1H, d, *J* = 9.2Hz, Ar*H*), 7.98 (1H, d, *J* = 8.8Hz, Ar*H*), 7.64 (2H, s, Ar*H*), 7.18 (2H, m, Ar*H*), 4.51 (4H, m, -C*H*$_2$-), 3.95 (3H, s, -OC*H*$_3$-); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ (ppm) = 156,35, 155.64, 150.52, 131.28, 129.59, 129.04, 127.52, 126.83, 125.05 , 122.02 (q, *J* = 287.3 Hz), 119.23, 116.85, 111.40, 106.61, 106,42, 66.08 (q, *J* = 31.9 Hz), 61.19; HR-APCI-TOF Ms: *m*/*z* 481.9936 (calcd *m*/*z* 481.9947 for $C_{19}H_{13}F_6BrO_3$ [M]).

3,6-Bis(trifluoroethoxy)-10-bromo-phenanthrene-9-ol



A solution of 3,6-bis(trifluoroethoxy)-10-bromo-9-methoxyphenanthrene (0.21 g, 0.44 mmol) was stirred in CH_2Cl_2 at -78°C under Ar atmosphere. 1 M BBr_3 in CH_2Cl_2 (0.65 mL) was added dropwise to the reaction mixture. The reaction mixture was slowly warmed to room temperature and stirred for overnight. The resulting mixture was poured into water and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried over Mg_2SO_4 and the solvent was evaporated to obtain 3,6-bis(trifluoroethoxy)-10-bromo-phenanthrene-9-ol. Yield >98%. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 8.28 (1H, d, *J* = 8.8Hz, Ar*H*), 8.03 (1H, d, *J* = 9.2Hz, Ar*H*), 7.86 (2H, s, Ar*H*), 7.27 (2H, d, *J* =9.6Hz, Ar*H*), 6.14 (1H, s, -O*H*), 4.55 (4H, m, -C*H*$_2$-). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ (ppm) = 156.76, 154,82, 145.90, 131.06, 128.22, 127.46, 126.53, 125.56, 124.72, 121.95, 120.85, 117.28, 116.55, 107.23, 106.67, 101.59, 66.27 (m); HR-APCI-TOF Ms: *m*/*z* 466.9740 (calcd *m*/*z* 466.9712 for $C_{18}H_{11}F_6O_3Br$ [M-H]).

3,6-Bis(trifluoroethoxy)-9-trifluoromethanesulfonate-10-trimehylsilyl-phenanthrene (2)

A solution of 3,6-bis(trifluoroethoxy)-10-bromo-phenanthrene-9-ol (0.21 g, 0.44 mmol) and hexamethyldisilazane (0.14 g, 0.87 mmol) in THF (7.7 mL) were stirred under reflux for 3 h under Ar atmosphere. After the solvent and excess hexamethyldisilazane were removed under reduce pressure, the residue was dissolved in dry THF (8.0 mL). To the mixture was added dropwise 1.6 mol/L *n*-BuLi solution (n-hexane) at -78°C under Ar atmosphere. After stirred for 45 min, trifluoromethanesulfonic anhydride (0.25 g, 0.87 mmol) was added. The reaction mixture was stirred for 20 min at -78°C and poured into $NaHCO_3$ *aq*. The mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Mg_2SO_4 and the solvent was evaporated. The crude product was purified by silica column chromatography (CH_2Cl_2) and recrystallization from CH_2Cl_2/hexane to obtain **2**. Yield 76%. ^{1}H NMR (MeOD, 400.13 MHz): δ(ppm) = 8.30 (2H, s, Ar*H*), 8.24 (1H, d, *J* = 9.2Hz, Ar*H*), 8.07 (1H, d, *J* = 9.2Hz, Ar*H*), 7.46 (2H, m, Ar*H*), 4.88 (4H, m, -C*H*$_2$-), 0.59 (9H, s, -C*H*$_3$); HR-APCI-TOF MS; *m*/*z* 594.0600 (calcd *m*/*z* 594.0573 for $C_{22}H_{19}F_9O_5SSi$ [M]).

Polymerization of 2 (1)

CsF (66 mg, 0.43 mmol), CuCN (1.0 mg, 11 μmol) and 18-crown 8 (0.23 g, 0.87 mmol) were dissolved in THF (1 mL) and stirred at room temperature for 10 min under Ar atmosphere. A solution of **2** (130 mg, 0.22 mmol) in THF (1.7 mL) was added to the reaction mixture and stirred for 48 h under Ar atmosphere. The reaction mixture was extracted with ethyl acetate. The combined organic phases were dried over Mg_2SO_4 and the solvent was evaporated. The crude product was purified by the reprecipitation from CH_2Cl_2/hexane to obtain **1**. Yield 45mg. ^{1}H NMR (MeOD, 400.13 MHz): δ(ppm) = 8.5-6.9 (6H, br, Ar*H*), 4.7-4.9 (4H, br, -OC*H*$_2$-).

6

CsF (20 mg, 0.13 mmol) and 18-crown 8 (0.23 g, 0.87 mmol) were dissolved in THF (0.4 mL) and stirred at room temperature for 10 min under Ar atmosphere. A solution of **2** (40 mg, 67 μmol) in THF (0.43 mL) was added to the reaction mixture and stirred for overnight under Ar atmosphere. The reaction mixture was extracted with ethyl acetate. The combined organic phases were dried over Mg_2SO_4 and the solvent was evaporated.

The crude product was purified by silica column chromatography (CH_2Cl_2) and recycling HPLC ($CHCl_3$) to obtain **6**. Yield 6.0%. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ(ppm) = 8.12 (6H, d, J = 8.8Hz, Ar*H*), 7.95 (6H, s, Ar*H*), 6.95 (6H, d, J = 9.2Hz, Ar*H*), 4.60 (6H, m, -O*C*H_2-); HR-APCI-TOF MS: *m*/*z* 1117.1081 (calcd *m*/*z* 1117.1828 for $C_{54}H_{30}F_{18}O_6$ [M+H]).

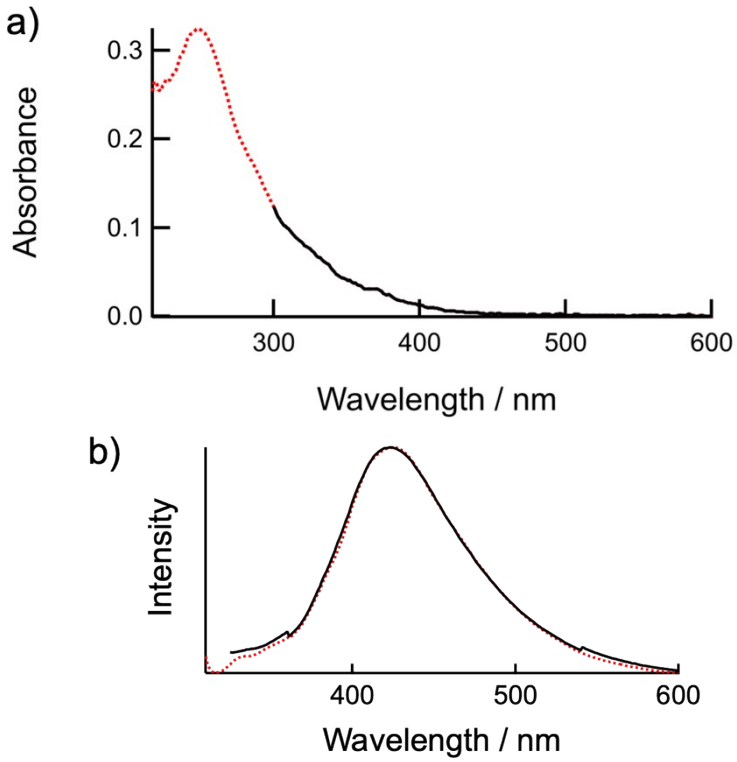


Fig. S1 a) Absorption and b) fluorescence spectra of **1** in toluene (black line) and ethanol (red dotted line) at room temperature.

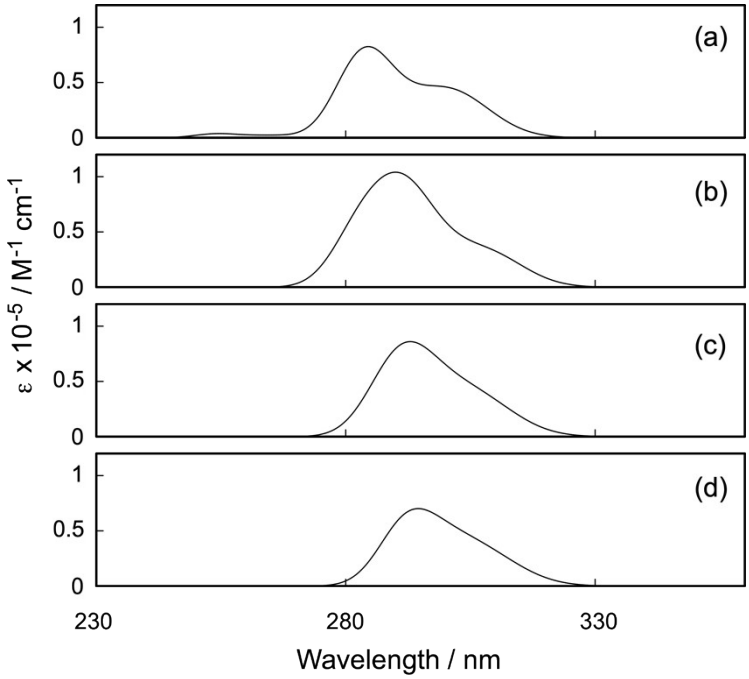


Fig. S2 Calculated absorption spectra (CAM B3LYP/6-31+G(d) level) of (a) trimer, (b) tetramer, (c) pentamer, and (d) hexamer.

Table S1. Transition energies, oscillator strength *f*, and configuration of trimer obtained from CAM B3LYP/6-31+G(d) calculation.

Energy/eV (nm)	*f*	Configuration (percentage of contribution)
3.97 (311.96)	0.0397	H→L+4 (28%), H→L (19%), H→L+2 (11%)
3.99 (311.01)	0.0632	H-1→L (56%), H→L+4 (11%)
4.02 (307.91)	0.0132	H-2→L+1 (45%), H-6→L (16%)
4.04 (307.05)	0.1259	H-1→L+2 (41%), H-2→L (17%), H-1→L+1 (10%)
4.14 (299.51)	0.1473	H-2→L (45%), H-1→L (19%), H-2→L+1 (11%)
4.22 (294.11)	0.0070	H→L (68%), H→L+4 (9%)
4.29 (288.83)	0.3440	H-1→L+3 (48%), H→L+5 (25%)
4.34 (285.82)	0.2118	H→L+5 (27%), H-1→L+3 (24%), H→L+3 (19%)

Table S2. Transition energies, oscillator strength *f*, and configuration of tetramer obtained from CAM B3LYP/6-31+G(d) calculation.

Energy/eV (nm)	*f*	Configuration (percentage of contribution)
3.93 (315.34)	0.1179	H-1→L (47%), H-3→L (32%)
3.96 (313.06)	0.0326	H→L+2 (31%), H-1→L+2 (21%)
4.00 (309.98)	0.1042	H→L+6 (25%), H→L (16%), H-1→L+2 (11%)
4.02 (308.55)	0.0056	H-3→L+1 (27%), H-1→L+1 (17%), H-8→L (13%), H-3→L+4 (10%)
4.04 (307.24)	0.0284	H-2→L+3 (10%), H-3→L+2 (10%)
4.14 (299.30)	0.0631	H-3→L (33%), H-2→L (22%),

		H-1→L (12%)
4.19 (296.00)	0.4447	H→L+4 (24%), H→L+3 (16%), H→L+5 (14%), H→L+1 (12%)
4.27 (290.07)	0.0643	H→L(53%)
4.29 (288.87)	0.2088	H-1→L+3 (25%), H-2→L+5 (19%)

Table S3. Transition energies, oscillator strength *f*, and configuration of pentamer obtained from CAM B3LYP/6-31+G(d) calculation.

Energy/eV (nm)	*f*	Configuration (percentage of contribution)
3.92 (316.27)	0.0430	H-1→L (59%), H-4→L (14%)
3.95 (314.08)	0.0077	H→L+2 (29%), H-2→L+2 (15%)
3.97 (312.31)	0.0781	H-2→L (22%), H-4→L (19%)
4.01 (309.29)	0.0161	H→L (7%), H→L+4 (7%), H-1→L+6 (7%)
4.03 (308.02)	0.0426	H-4→L+1 (25%)
4.04 (307.22)	0.1268	H-4→L (20%), H-1→L+1 (10%)
4.07 (304.43)	0.0260	H-4→L+1 (11%), H-2→L+1 (10%)
4.18 (296.50)	0.3782	H→L+3 (16%), H-2→L+3 (10%)
4.23 (293.15)	0.1280	H→L+6 (8%), H-1→L+7 (6%)

Table S4. Transition energies, oscillator strength *f*, and configuration of hexamer obtained from CAM B3LYP/6-31+G(d) calculation.

Energy/eV (nm)	*f*	Configuration (percentage of contribution)
3.91 (317.47)	0.0483	H→L (22%), H-5→L (18%), H-2→L (16%)
3.94 (314.30)	0.0196	H-1→L+2 (18%), H-1→L+3 (17%)
3.97 (311.94)	0.0371	H-2→L (18%), H-3→L (9%)
3.99 (311.02)	0.0023	H-5→L+1 (13%)
4.00 (310.21)	0.0094	H→L (13%)
4.01 (309.10)	0.0593	H-3→L (11%)
4.03 (307.55)	0.1215	H-5→L (15%), H→L+8 (10%)
4.07 (304.28)	0.0519	H-3→L (10%),H-2→L (9%)
4.18 (296.49)	0.2664	H-1→L+3 (23%),H-1→L+5 (10%)
4.20 (295.24)	0.1343	H→L (30%)

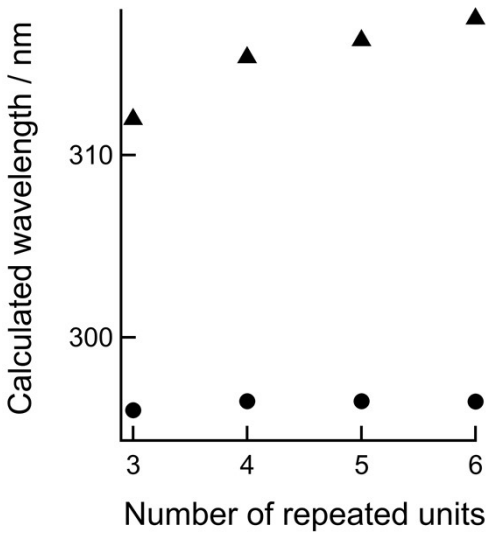


Fig. S3 Dependence of calculated wavelengths at the lowest transition energy (▲) and the highest oscillator strength (●) (CAM B3LYP/6-31+G(d)) on the g number of repeated units in oligomers.

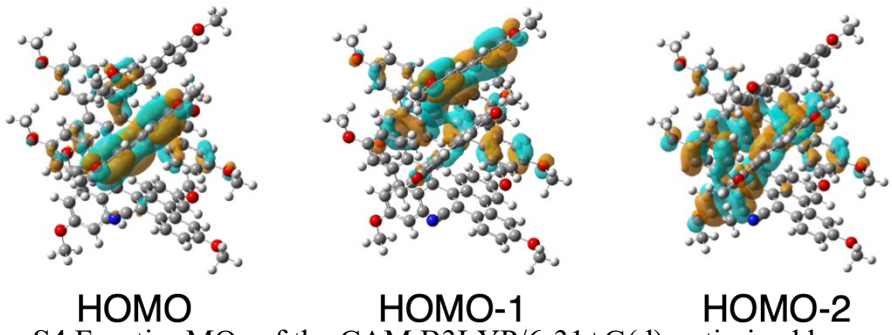


Fig. S4 Frontier MOs of the CAM B3LYP/6-31+G(d) optimized hexamer.

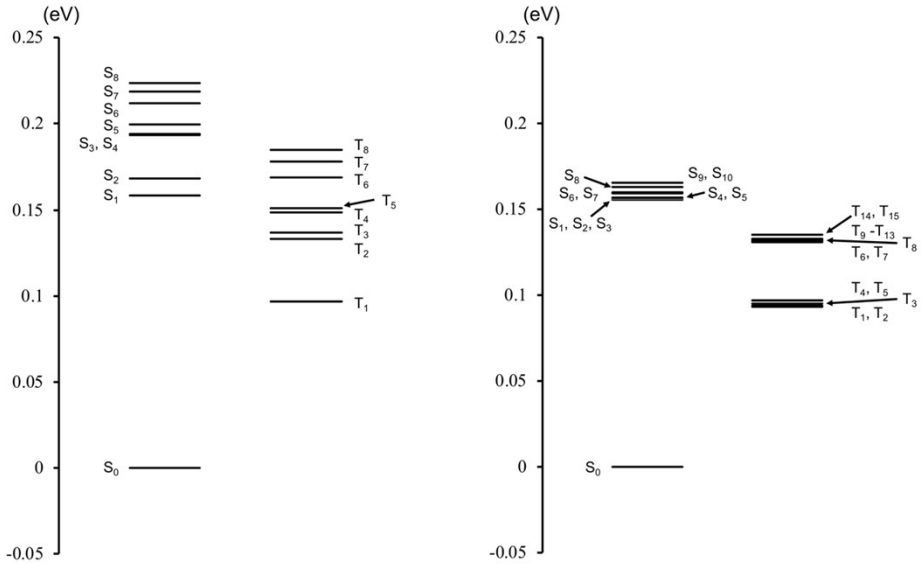


Fig. S5 Calculated energy levels of excited states of phenanthrene (left) and pentamer (right).

Table S5. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for pentamer obtained from CAM B3LYP/6-311+G(d,p) calculation.

Excited state	E_g [eV]	E_g [nm]	f	Transition			Coefficient
S1	4.2344	292.81	0.0039	HOMO-8	->	LUMO+2	0.18150
				HOMO-7	->	LUMO+7	-0.15652
				HOMO-5	->	LUMO	0.14293
				HOMO-4	->	LUMO	-0.17777
				HOMO-4	->	LUMO+9	-0.11258
				HOMO-3	->	LUMO+1	0.10096
				HOMO-3	->	LUMO+5	-0.15158
				HOMO-2	->	LUMO+5	-0.11933
				HOMO-2	->	LUMO+8	-0.18575
S2	4.2407	292.37	0.0007	HOMO-9	->	LUMO+1	-0.20465
				HOMO-9	->	LUMO+2	0.10309
				HOMO-8	->	LUMO	-0.11526
				HOMO-7	->	LUMO+5	-0.11357
				HOMO-6	->	LUMO+3	0.10527
				HOMO-6	->	LUMO+4	0.13290
				HOMO-5	->	LUMO+1	-0.11336
				HOMO-5	->	LUMO+8	-0.13676
				HOMO-4	->	LUMO+5	-0.12451
				HOMO-3	->	LUMO	-0.19218
				HOMO-3	->	LUMO+4	0.11177
				HOMO-3	->	LUMO+7	-0.15519
				HOMO-2	->	LUMO+9	-0.15930
				HOMO-1	->	LUMO+1	-0.12585
				HOMO-1	->	LUMO+6	-0.14169
				HOMO	->	LUMO	0.25083
				HOMO	->	LUMO+3	-0.22960
S3	4.2484	291.83	0.0031	HOMO-8	->	LUMO	0.14900
				HOMO-8	->	LUMO+7	-0.17852
				HOMO-7	->	LUMO+2	0.20458
				HOMO-7	->	LUMO+5	0.11130
				HOMO-6	->	LUMO	0.10019
				HOMO-6	->	LUMO+3	0.10878
				HOMO-5	->	LUMO+5	0.10001
				HOMO-4	->	LUMO+2	-0.10956
				HOMO-4	->	LUMO+6	-0.13056
				HOMO-3	->	LUMO	-0.16010
				HOMO-2	->	LUMO+3	0.14439

				HOMO-2	->	LUMO+4	-0.19422
				HOMO-1	->	LUMO+1	0.11321
				HOMO-1	->	LUMO+5	-0.15472
				HOMO-1	->	LUMO+6	0.15225
				HOMO-1	->	LUMO+8	-0.17239
				HOMO	->	LUMO+4	-0.17363
				HOMO	->	LUMO+9	0.12786
S4	4.2634	290.81	0.0007	HOMO-9	->	LUMO+1	-0.23707
				HOMO-9	->	LUMO+2	0.12176
				HOMO-9	->	LUMO+5	-0.13888
				HOMO-8	->	LUMO	0.10685
				HOMO-7	->	LUMO+1	-0.12987
				HOMO-6	->	LUMO	-0.15694
				HOMO-6	->	LUMO+3	0.10548
				HOMO-6	->	LUMO+7	-0.11919
				HOMO-5	->	LUMO+1	0.11308
				HOMO-5	->	LUMO+8	0.11993
				HOMO-3	->	LUMO+3	0.19860
				HOMO-3	->	LUMO+4	0.11572
				HOMO-2	->	LUMO	0.17013
				HOMO-2	->	LUMO+3	-0.15040
				HOMO-1	->	LUMO+2	0.11095
				HOMO	->	LUMO	0.10596
				HOMO	->	LUMO+4	-0.18209
				HOMO	->	LUMO+9	-0.11401
S5	4.2669	290.57	0.0014	HOMO-8	->	LUMO+5	0.14363
				HOMO-7	->	LUMO	0.19958
				HOMO-6	->	LUMO+2	0.14103
				HOMO-5	->	LUMO+3	-0.15425
				HOMO-5	->	LUMO+7	-0.16604
				HOMO-4	->	LUMO	0.14434
				HOMO-4	->	LUMO+3	-0.11216
				HOMO-4	->	LUMO+4	0.11356
				HOMO-4	->	LUMO+9	0.10193
				HOMO-3	->	LUMO+1	-0.13140
				HOMO-3	->	LUMO+2	-0.10266
				HOMO-3	->	LUMO+6	0.12262
				HOMO-2	->	LUMO+1	0.10525
				HOMO-2	->	LUMO+6	0.21003
				HOMO-1	->	LUMO+4	-0.13728
				HOMO-1	->	LUMO+9	0.15569
				HOMO	->	LUMO+5	-0.11836
				HOMO	->	LUMO+8	-0.22182
S6	4.3347	286.03	0.0095	HOMO-5	->	LUMO+5	-0.1015
				HOMO-5	->	LUMO+6	-0.10401
				HOMO-4	->	LUMO+1	0.11591
				HOMO-3	->	LUMO	0.13829
				HOMO-2	->	LUMO+7	-0.15571
				HOMO-1	->	LUMO+1	0.17847
				HOMO-1	->	LUMO+2	0.23908
				HOMO-1	->	LUMO+6	-0.11062
				HOMO	->	LUMO	0.43344
				HOMO	->	LUMO+3	0.19348
S7	4.3488	285.1	0.3257	HOMO-4	->	LUMO+3	0.10235
				HOMO-4	->	LUMO+7	0.11043
				HOMO-3	->	LUMO+1	-0.16047
				HOMO-2	->	LUMO+5	0.14389
				HOMO-1	->	LUMO	0.31573
				HOMO	->	LUMO+1	0.38398
				HOMO	->	LUMO+2	0.12526
				HOMO	->	LUMO+6	-0.14751
S8	4.4302	279.86	0.1471	HOMO-9	->	LUMO+3	0.10586
				HOMO-7	->	LUMO+4	0.13127
				HOMO-6	->	LUMO+1	0.13741
				HOMO-6	->	LUMO+5	0.13506
				HOMO-4	->	LUMO	-0.10972
				HOMO-3	->	LUMO+1	0.21101
				HOMO-2	->	LUMO+2	0.17940
				HOMO-1	->	LUMO	0.24263
				HOMO-1	->	LUMO+3	0.11074
				HOMO-1	->	LUMO+7	-0.15923

				HOMO	->	LUMO+1	-0.22448
				HOMO	->	LUMO+2	0.32835
S9	4.4999	275.53	0.0892	HOMO-8	->	LUMO+4	0.12283
				HOMO-7	->	LUMO+6	-0.13606
				HOMO-6	->	LUMO	0.14628
				HOMO-5	->	LUMO+2	-0.11182
				HOMO-4	->	LUMO+2	-0.13117
				HOMO-4	->	LUMO+8	-0.12476
				HOMO-2	->	LUMO	0.33402
				HOMO-2	->	LUMO+3	0.15454
				HOMO-1	->	LUMO+2	0.17739
				HOMO-1	->	LUMO+5	0.19375
				HOMO	->	LUMO+7	-0.22182
S10	4.5073	275.07	0.0050	HOMO-9	->	LUMO+4	-0.12605
				HOMO-7	->	LUMO+3	-0.12954
				HOMO-6	->	LUMO+1	-0.16411
				HOMO-5	->	LUMO	-0.18586
				HOMO-4	->	LUMO	-0.16707
				HOMO-4	->	LUMO+3	-0.12133
				HOMO-3	->	LUMO+2	0.14185
				HOMO-2	->	LUMO+1	0.26081
				HOMO-2	->	LUMO+2	0.16179
				HOMO-2	->	LUMO+6	-0.10020
				HOMO-1	->	LUMO+7	-0.18692
				HOMO	->	LUMO+5	0.24594
T1	2.5451	487.14	0.0000	HOMO-9	->	LUMO+3	-0.11161
				HOMO-9	->	LUMO+4	-0.11167
				HOMO-8	->	LUMO+6	-0.11032
				HOMO-6	->	LUMO+1	-0.11603
				HOMO-6	->	LUMO+2	0.12685
				HOMO-6	->	LUMO+8	0.1051
				HOMO-5	->	LUMO+9	0.11686
				HOMO-4	->	LUMO+7	0.16562
				HOMO-3	->	LUMO+1	-0.13814
				HOMO-3	->	LUMO+2	0.11442
				HOMO-2	->	LUMO+5	0.19356
				HOMO-2	->	LUMO+8	-0.11197
				HOMO-1	->	LUMO	0.24336
				HOMO	->	LUMO+1	0.25084
				HOMO	->	LUMO+2	0.13254
				HOMO	->	LUMO+6	-0.12581
T2	2.5545	485.36	0.0000	HOMO-8	->	LUMO+3	-0.10298
				HOMO-8	->	LUMO+4	0.12465
				HOMO-7	->	LUMO+8	0.11601
				HOMO-6	->	LUMO+9	-0.11761
				HOMO-5	->	LUMO+5	-0.12558
				HOMO-5	->	LUMO+6	-0.14647
				HOMO-4	->	LUMO+1	0.12480
				HOMO-4	->	LUMO+5	-0.14557
				HOMO-4	->	LUMO+8	0.11471
				HOMO-2	->	LUMO+7	-0.22296
				HOMO-1	->	LUMO+1	0.11241
				HOMO-1	->	LUMO+2	0.25314
				HOMO	->	LUMO	0.29791
				HOMO	->	LUMO+3	0.12585
T3	2.5902	478.68	0.0000	HOMO-9	->	LUMO	-0.11320
				HOMO-9	->	LUMO+3	0.15857
				HOMO-9	->	LUMO+4	0.12799
				HOMO-9	->	LUMO+9	0.10367
				HOMO-7	->	LUMO+4	0.14148
				HOMO-6	->	LUMO+1	0.19322
				HOMO-6	->	LUMO+5	0.16530
				HOMO-3	->	LUMO+1	0.22682
				HOMO-3	->	LUMO+5	0.10616
				HOMO-2	->	LUMO+1	-0.14585
				HOMO-2	->	LUMO+2	0.15569
				HOMO-1	->	LUMO	0.14106
				HOMO-1	->	LUMO+7	-0.11270
				HOMO	->	LUMO+1	-0.14964
				HOMO	->	LUMO+2	0.22835
T4	2.6405	469.55	0.0000	HOMO-8	->	LUMO+4	0.11852

				HOMO-8	->	LUMO+9	-0.11404
				HOMO-7	->	LUMO+6	-0.13515
				HOMO-6	->	LUMO	0.11276
				HOMO-5	->	LUMO+2	-0.10419
				HOMO-5	->	LUMO+6	0.10427
				HOMO-4	->	LUMO+2	-0.15055
				HOMO-4	->	LUMO+8	-0.12515
				HOMO-3	->	LUMO+3	0.11308
				HOMO-2	->	LUMO	0.24737
				HOMO-2	->	LUMO+3	0.12504
				HOMO-1	->	LUMO+2	0.13539
				HOMO-1	->	LUMO+5	0.19977
				HOMO	->	LUMO+7	-0.22560
T5	2.6468	468.43	0.0000	HOMO-8	->	LUMO+8	0.11974
				HOMO-7	->	LUMO+3	-0.12211
				HOMO-6	->	LUMO+1	-0.11237
				HOMO-6	->	LUMO+6	-0.11340
				HOMO-5	->	LUMO	-0.16489
				HOMO-5	->	LUMO+9	-0.12965
				HOMO-4	->	LUMO	-0.17231
				HOMO-4	->	LUMO+3	-0.12469
				HOMO-3	->	LUMO+2	0.11687
				HOMO-2	->	LUMO+1	0.17951
				HOMO-2	->	LUMO+2	0.17224
				HOMO-1	->	LUMO+7	-0.22176
				HOMO	->	LUMO+5	0.22846
				HOMO	->	LUMO+8	-0.10183
T6	3.5667	347.62	0.0000	HOMO-12	->	LUMO+5	-0.10872
				HOMO-10	->	LUMO+7	0.12010
				HOMO-8	->	LUMO+2	0.11220
				HOMO-8	->	LUMO+6	0.12242
				HOMO-6	->	LUMO+6	-0.12540
				HOMO-5	->	LUMO+3	0.11418
				HOMO-5	->	LUMO+4	-0.10112
				HOMO-5	->	LUMO+9	-0.1011
				HOMO-2	->	LUMO+2	-0.11231
				HOMO-2	->	LUMO+6	-0.14152
				HOMO-1	->	LUMO	0.16312
				HOMO-1	->	LUMO+4	0.14669
				HOMO-1	->	LUMO+9	-0.10260
T7	3.5688	347.41	0.0000	HOMO-12	->	LUMO+7	0.10079
				HOMO-10	->	LUMO+2	-0.10687
				HOMO-8	->	LUMO+3	0.12211
				HOMO-8	->	LUMO+4	-0.11856
				HOMO-7	->	LUMO+2	0.10822
				HOMO-7	->	LUMO+8	-0.10452
				HOMO-5	->	LUMO+6	0.14097
				HOMO-3	->	LUMO+9	-0.12355
				HOMO-2	->	LUMO+4	0.11490
				HOMO-1	->	LUMO+6	-0.19465
				HOMO	->	LUMO	0.21072
T8	3.5893	345.43	0.0000	HOMO-9	->	LUMO	-0.15886
				HOMO-9	->	LUMO+3	0.27467
				HOMO-9	->	LUMO+4	0.24386
				HOMO-9	->	LUMO+9	0.10165
				HOMO-6	->	LUMO+1	-0.13777
				HOMO-3	->	LUMO+8	0.10267
				HOMO	->	LUMO+1	0.22225
T9	3.6008	344.32	0.0000	HOMO-11	->	LUMO	0.10970
				HOMO-11	->	LUMO+7	0.11933
				HOMO-5	->	LUMO+5	-0.11888
				HOMO-5	->	LUMO+6	-0.15164
				HOMO-4	->	LUMO+8	-0.10912
				HOMO-4	->	LUMO+19	-0.10280
				HOMO-2	->	LUMO+3	0.10757
				HOMO-2	->	LUMO+9	-0.16506
				HOMO-2	->	LUMO+23	-0.10391
				HOMO	->	LUMO+3	-0.10327
				HOMO	->	LUMO+9	0.11022
				HOMO	->	LUMO+23	0.10142
T10	3.6105	343.4	0.0000	HOMO-17	->	LUMO+3	-0.10695

				HOMO-13	->	LUMO+1	0.14930
				HOMO-13	->	LUMO+2	-0.11562
				HOMO-9	->	LUMO+1	0.13737
				HOMO-9	->	LUMO+34	0.10795
				HOMO-6	->	LUMO+3	0.15837
				HOMO-6	->	LUMO+4	0.13114
				HOMO-6	->	LUMO+14	0.12207
				HOMO-5	->	LUMO+8	-0.10180
				HOMO-4	->	LUMO+6	0.13057
				HOMO-3	->	LUMO+4	0.12041
				HOMO-3	->	LUMO+9	0.14082
				HOMO-3	->	LUMO+14	0.11741
				HOMO-2	->	LUMO+3	-0.11020
				HOMO	->	LUMO+3	-0.12812
				HOMO	->	LUMO+9	-0.10283
T11	3.6113	343.32	0.0000	HOMO-10	->	LUMO	-0.12164
				HOMO-9	->	LUMO+3	-0.10444
				HOMO-9	->	LUMO+4	-0.12102
				HOMO-6	->	LUMO+5	0.10105
				HOMO-5	->	LUMO	0.10439
				HOMO-4	->	LUMO+3	-0.10398
				HOMO-4	->	LUMO+9	0.13946
				HOMO-3	->	LUMO+1	0.10282
				HOMO-2	->	LUMO+8	0.12261
				HOMO-2	->	LUMO+19	0.11627
				HOMO-1	->	LUMO+3	-0.1077
				HOMO	->	LUMO+6	-0.15681
T12	3.6157	342.91	0.0000	HOMO-13	->	LUMO+1	0.12754
				HOMO-9	->	LUMO+1	0.10367
				HOMO-6	->	LUMO+9	0.18183
				HOMO-5	->	LUMO+8	0.14841
				HOMO-4	->	LUMO+6	-0.17081
				HOMO-3	->	LUMO+3	0.19340
				HOMO-2	->	LUMO+4	-0.12527
				HOMO-1	->	LUMO+2	0.12030
				HOMO	->	LUMO	0.13341
				HOMO	->	LUMO+4	-0.11698
T13	3.6157	342.9	0.0000	HOMO-9	->	LUMO+3	-0.11051
				HOMO-9	->	LUMO+9	-0.10944
				HOMO-8	->	LUMO+6	0.15154
				HOMO-7	->	LUMO+4	-0.11128
				HOMO-7	->	LUMO+9	0.10213
				HOMO-6	->	LUMO+8	-0.14924
				HOMO-5	->	LUMO+3	0.13855
				HOMO-5	->	LUMO+7	0.10030
				HOMO-5	->	LUMO+9	-0.11872
				HOMO-4	->	LUMO	0.13728
				HOMO-4	->	LUMO+4	0.11087
				HOMO-3	->	LUMO+5	0.10782
				HOMO-3	->	LUMO+8	0.11237
				HOMO-1	->	LUMO	0.12193
				HOMO-1	->	LUMO+4	-0.11274
				HOMO	->	LUMO+2	0.18571
				HOMO	->	LUMO+5	-0.10555
T14	3.6738	337.48	0.0000	HOMO-8	->	LUMO+4	-0.22503
				HOMO-8	->	LUMO+9	0.16568
				HOMO-7	->	LUMO+6	0.23749
				HOMO-6	->	LUMO+3	0.11391
				HOMO-6	->	LUMO+4	-0.13148
				HOMO-5	->	LUMO+8	-0.12490
				HOMO-4	->	LUMO+2	-0.14247
				HOMO-3	->	LUMO	0.11878
				HOMO-2	->	LUMO	0.15902
				HOMO-1	->	LUMO+2	0.13661
				HOMO-1	->	LUMO+5	0.12653
				HOMO	->	LUMO+7	-0.16761
T15	3.6808	336.84	0.0000	HOMO-9	->	LUMO+4	0.10634
				HOMO-8	->	LUMO+5	-0.14204
				HOMO-8	->	LUMO+6	0.15500
				HOMO-8	->	LUMO+8	-0.16609
				HOMO-7	->	LUMO+3	0.14857

				HOMO-7	->	LUMO+4	-0.22198
				HOMO-6	->	LUMO+2	0.12022
				HOMO-6	->	LUMO+6	0.13838
				HOMO-5	->	LUMO+9	0.13707
				HOMO-4	->	LUMO	-0.13418
				HOMO-3	->	LUMO+6	-0.14854
				HOMO-2	->	LUMO+2	0.13342
				HOMO-1	->	LUMO+7	-0.16335
				HOMO	->	LUMO+5	0.13326

Table S6. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for phenanthrene obtained from CAM B3LYP/6-311+G(d,p) calculation..

Excited state	E_g [eV]	E_g [nm]	*f*	Transition			Coefficient
S1	4.3062	287.92	0.0018	HOMO-1	->	LUMO	0.44256
				HOMO	->	LUMO+1	0.52689
S2	4.5808	270.66	0.0606	HOMO-1	->	LUMO+1	-0.38039
				HOMO	->	LUMO	0.58532
S3	5.2733	235.12	0.7223	HOMO-3	->	LUMO	-0.12483
				HOMO-2	->	LUMO+1	-0.13126
				HOMO-1	->	LUMO+1	0.50722
				HOMO-1	->	LUMO+3	0.28177
				HOMO	->	LUMO	0.33312
S4	5.2788	234.87	0.1665	HOMO-1	->	LUMO	0.49035
				HOMO	->	LUMO+1	-0.44690
				HOMO	->	LUMO+3	-0.22312
S5	5.4367	228.05	0.3112	HOMO-3	->	LUMO	0.18292
				HOMO-2	->	LUMO+1	0.39115
				HOMO-1	->	LUMO+1	0.28345
				HOMO-1	->	LUMO+3	-0.37577
				HOMO	->	LUMO	0.17230
				HOMO	->	LUMO+8	-0.20795
S6	5.7674	214.98	0.1286	HOMO-2	->	LUMO	0.12033
				HOMO-1	->	LUMO	0.22026
				HOMO	->	LUMO+3	0.63190
S7	5.9454	208.54	0.0048	HOMO	->	LUMO+2	0.61542
				HOMO	->	LUMO+4	-0.23710
				HOMO	->	LUMO+7	-0.11775
				HOMO	->	LUMO+11	0.12992
S8	6.0917	203.53	0.0046	HOMO-3	->	LUMO+1	-0.15897
				HOMO-2	->	LUMO	0.63125
				HOMO-1	->	LUMO+8	0.20686
T1	2.636	470.35	0.0000	HOMO-3	->	LUMO+8	0.13244
				HOMO-2	->	LUMO+3	-0.18760
				HOMO-1	->	LUMO+1	-0.36377
				HOMO	->	LUMO	0.55857
				HOMO-1	<-	LUMO+1	-0.10364
				HOMO	<-	LUMO	0.12962
T2	3.6158	342.9	0.0000	HOMO-3	->	LUMO+1	0.19282
				HOMO-2	->	LUMO	-0.29139
				HOMO-2	->	LUMO+8	-0.13359
				HOMO-1	->	LUMO	-0.18912
				HOMO-1	->	LUMO+8	-0.17131
				HOMO	->	LUMO+1	0.44248
				HOMO	->	LUMO+3	0.26065
T3	3.7302	332.38	0.0000	HOMO-4	->	LUMO	0.10904
				HOMO-3	->	LUMO+8	-0.11957
				HOMO-1	->	LUMO+1	0.54189
				HOMO	->	LUMO	0.37059
				HOMO	->	LUMO+8	-0.10232
T4	4.0428	306.68	0.0000	HOMO-3	->	LUMO+1	-0.13402
				HOMO-2	->	LUMO	0.27797
				HOMO-1	->	LUMO	-0.30728
				HOMO-1	->	LUMO+8	0.10354
				HOMO	->	LUMO+1	0.37928
				HOMO	->	LUMO+3	-0.35165
T5	4.1038	302.12	0.0000	HOMO-3	->	LUMO+3	-0.10921
				HOMO-1	->	LUMO	0.57914
				HOMO	->	LUMO+1	0.34841

				HOMO	->	LUMO+3	-0.11739
T6	4.5988	269.6	0.0000	HOMO-4	->	LUMO	0.11810
				HOMO-3	->	LUMO	-0.24575
				HOMO-2	->	LUMO+1	0.38685
				HOMO-1	->	LUMO+1	-0.12959
				HOMO-1	->	LUMO+3	0.38309
				HOMO	->	LUMO+8	-0.27057
T7	4.8497	255.65	0.0000	HOMO-3	->	LUMO+1	0.44073
				HOMO-2	->	LUMO	0.17452
				HOMO-1	->	LUMO+8	-0.37893
				HOMO-1	->	LUMO+13	0.12964
				HOMO	->	LUMO+3	-0.26053
T8	5.0266	246.66	0.0000	HOMO-4	->	LUMO	-0.24137
				HOMO-3	->	LUMO	-0.15887
				HOMO-2	->	LUMO+1	-0.22698
				HOMO-2	->	LUMO+3	-0.19969
				HOMO-1	->	LUMO+1	0.12140
				HOMO-1	->	LUMO+3	0.46128
				HOMO	->	LUMO+8	0.23578
				HOMO	->	LUMO+23	0.12231