Electronic Supplementary Material (ESI) for RSC Advances.

Corrole-BODIPY Conjugates: Enhancing the Fluorescence and Phosphorescence of the Corrole Complex via Efficient Through Bond Energy Transfer

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1. Experimental details

1.1 Methods

MALDI-TOF mass spectral data were measured on a Bruker Daltonics autoflex^{II}. HPLC-MS data were measured on a Agilent 6540Q-TOF with CH_3OH as the solvent. The ^1H NMR spectroscopic measurements were made by using a Bruker 500 MHz spectrometer with $CDCl_3$ as the solvent. Fluorescence and phosphorescence spectral and lifetime measurements were carried out on a Hitachi F–4600 and Edinberge fls920 fluorometer. UV-visible absorption spectra were recorded with a Shimadzu UV–2550 spectrometer.

1.2 Synthetic details

2: Compound **2** was synthesized according to the literature methods.[1] The data were in full accordance with the literature.

2,2'-((perfluorophenyl)methylene)bis(1H-pyrrole): 17 ml of redistilled pyrrole and 10 mmol of pentafluorobenzaldehyde were injected into a 100 ml flask under Ar. Several drops of trifluoroacetic acid were added to the solution. After stirring for 5 min, the reaction mixture was quenched with 0.1 M NaOH solution and extracted with ethyl acetate. The organic layer was washed with water and dried with anhydrous Na_2SO_4. Then the solvent and residual pyrrole was removed under reduced pressure, and the residue was purified by silica gel column chromatography using TCM as the eluent to give a pale solid (1.5 g, yield: 48%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (br, 2H, NH), 6.74 (q, J =5.5 Hz, 2H), 6.16 (q, J = 11 Hz, 2H), 6.02 (s, 2H), 5.90 (s, 1H).

3: Dipyrromethane (1 mmol, 312 mg) and 4-Hydroxybenzaldehyde (0.5 mmol, 61 mg) were dissolved in MeOH (50 ml). A solution of $HCl_{(aq)}$ (36%, 2.5 ml) in H_2O (50 ml) was then added, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed with twice with water, dried (Na_2SO_4), filtered, and diluted to 250 ml with $CHCl_3$. DDQ (350 mg, 1.5 mmol) was added, and the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using TCM as the eluent to give the product (80 mg, yield: 21%). ^1H NMR (500 MHz, $CDCl_3$) δ 9.11 (s, 2H), 8.72 (s, 4H), 8.57 (s, 2H), 8.04 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H). MALDI-TOF-MS m/z: calcd for $C_{37}H_{16}BF_{10}N_4O$: 722.12, found: 722.30.

4: Corrole **3** (20 mg, 0.028 mmol) and BODIPY **1** (8 mg, 0.028 mmol) were dissolved in 20 ml of dichloromethane. The reaction mixture was purged with Ar and 100 µl triethylamine was then added to the solution. After stirring for 2 h, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using dichloromethane/petroleum ether (1:1; v/v) as the eluent to give the product (26 mg, yield: 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 2H), 8.79 (s, 2H), 8.72 (s, 2H), 8.59 (s, 2H), 8.30 (d, J = 4 Hz, 2H), 7.87 (s, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.13 (d, J = 4 Hz, 2H), 6.60 (d, J = 2.8 Hz, 2H). MALDI-TOF-MS m/z: calcd for $C_{46}H_{21}BF_{12}N_6O$: 912.1678, found: 911.275.

5: Corrole 5 was synthesized according to the literature method.[2] ^1H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, J = 4.0 Hz, 2H), 8.54 (s, 4H), 8.19 (d, J = 4.0 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 6.09 (t, J = 7.6 Hz, 2H), 5.15 (t, J = 7.2 Hz, 4H), 1.73 (d, J = 5.6 Hz, 4H).

6: Iridium corrole **5** (30 mg, 0.028 mmol) and BODIPY **1** (8 mg, 0.028 mmol) were dissolved in 20 ml of dichloromethane. The reaction mixture was purged with Ar and 100 µl of triethylamine was then added to the solution. After stirring for 2 h, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using trichloromethane as the eluent to give the product (34 mg, yield: 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, J = 4.4 Hz, 2H), 8.61 (d, J = 4.4 Hz, 2H), 8.52 (d, J = 4.8 Hz, 2H), 8.19 (d, J = 4.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H), 7.82 (s 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 4.0 Hz, 2H), 6.54 (d, J = 2.4 Hz, 2H), 6.10 (t, J = 7.6 Hz, 2H), 5.17 (t, J = 7.2 Hz, 4H), 1.73 (d, J = 5.6 Hz, 4H). HPLC-MS m/z: calcd for $C_{56}H_{28}BF_{12}IrN_8O$: 1260.1917, found: 1260.1929.

2. Supplementary data

2.1

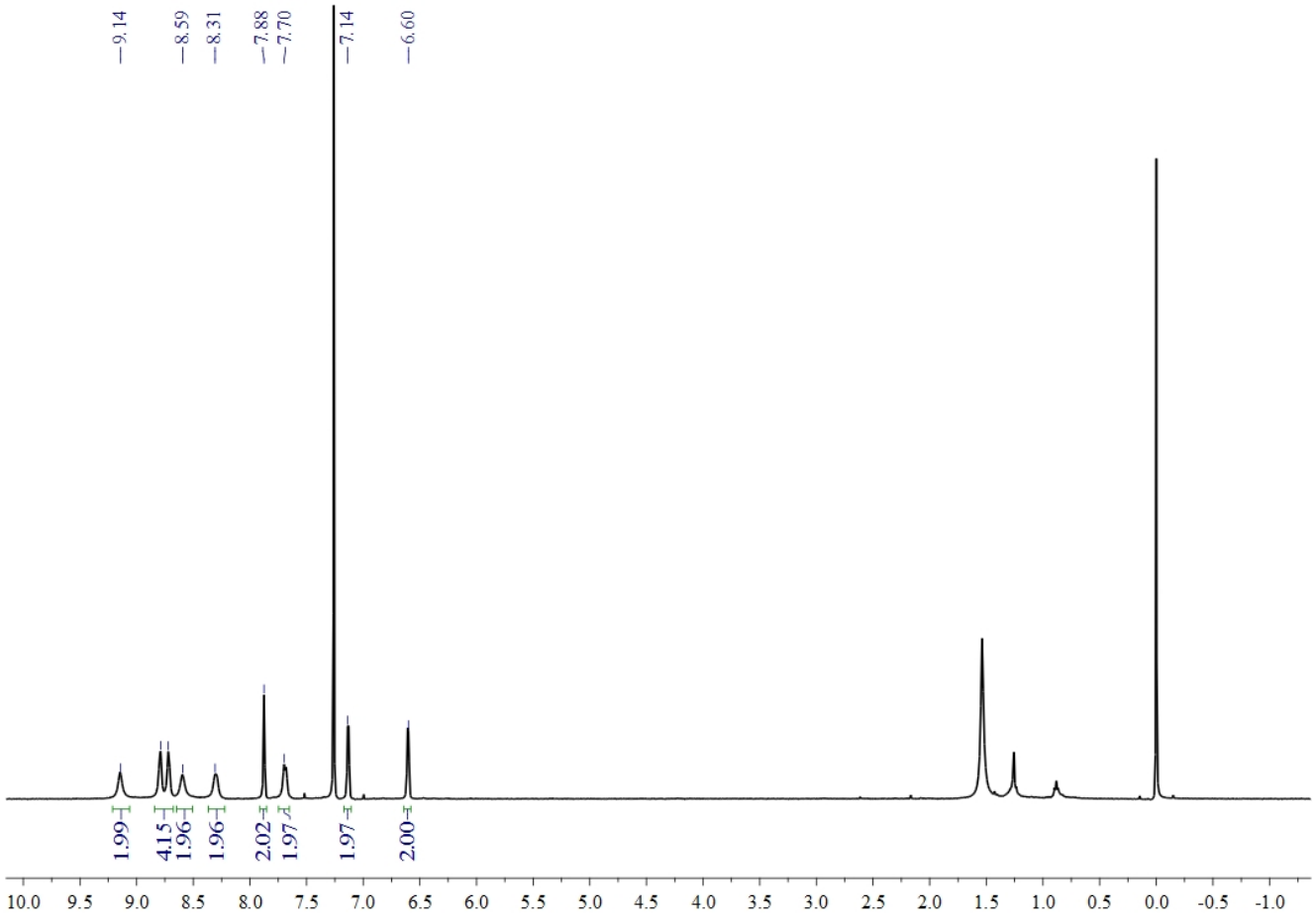


Figure S1. ^{1}H NMR spectrum of conjugate **4** (in $CDCl_3$, 298 K).

2.2

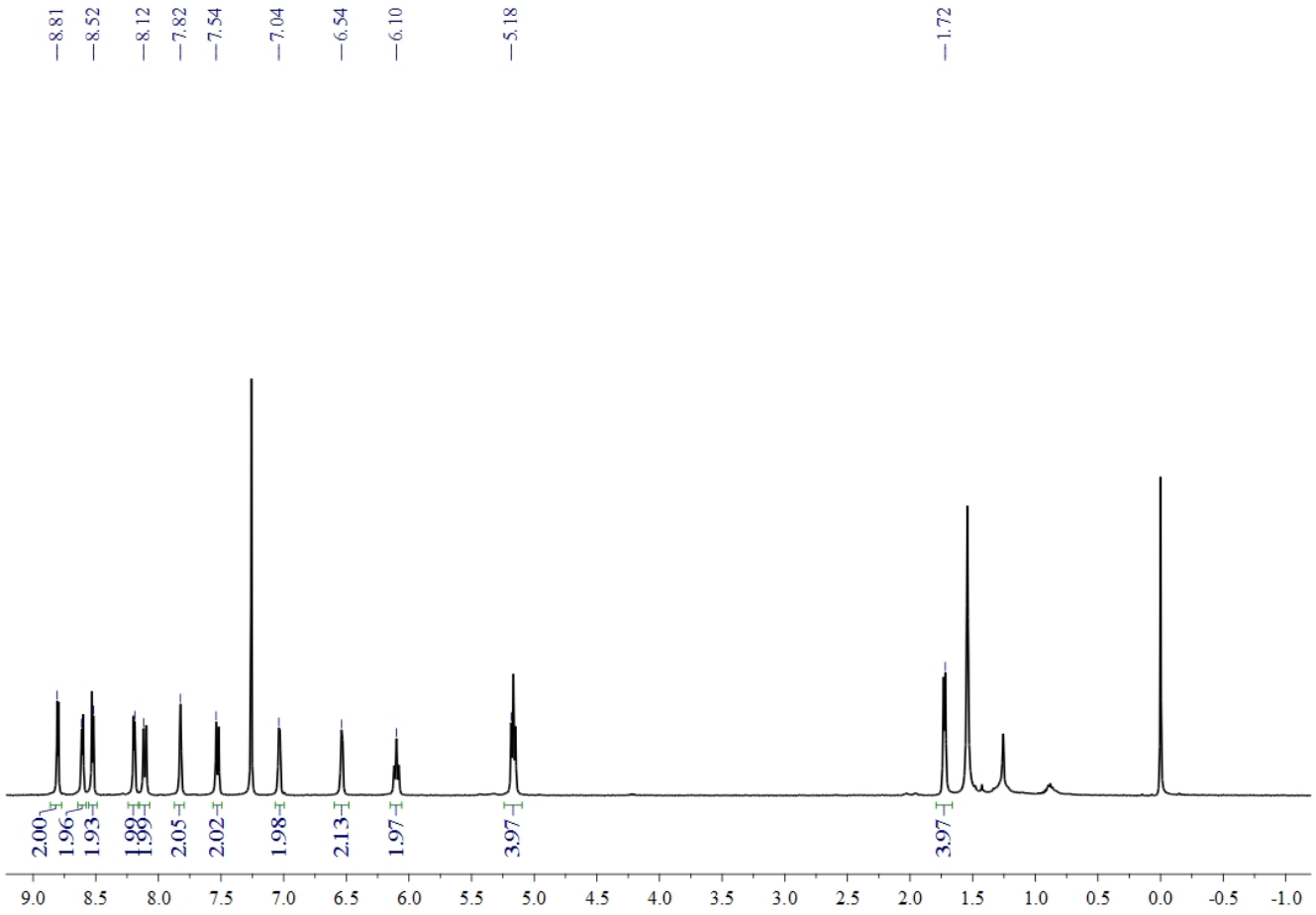


Figure S2. ^{1}H NMR spectrum of conjugate **6** (in $CDCl_3$, 298 K).

2.3

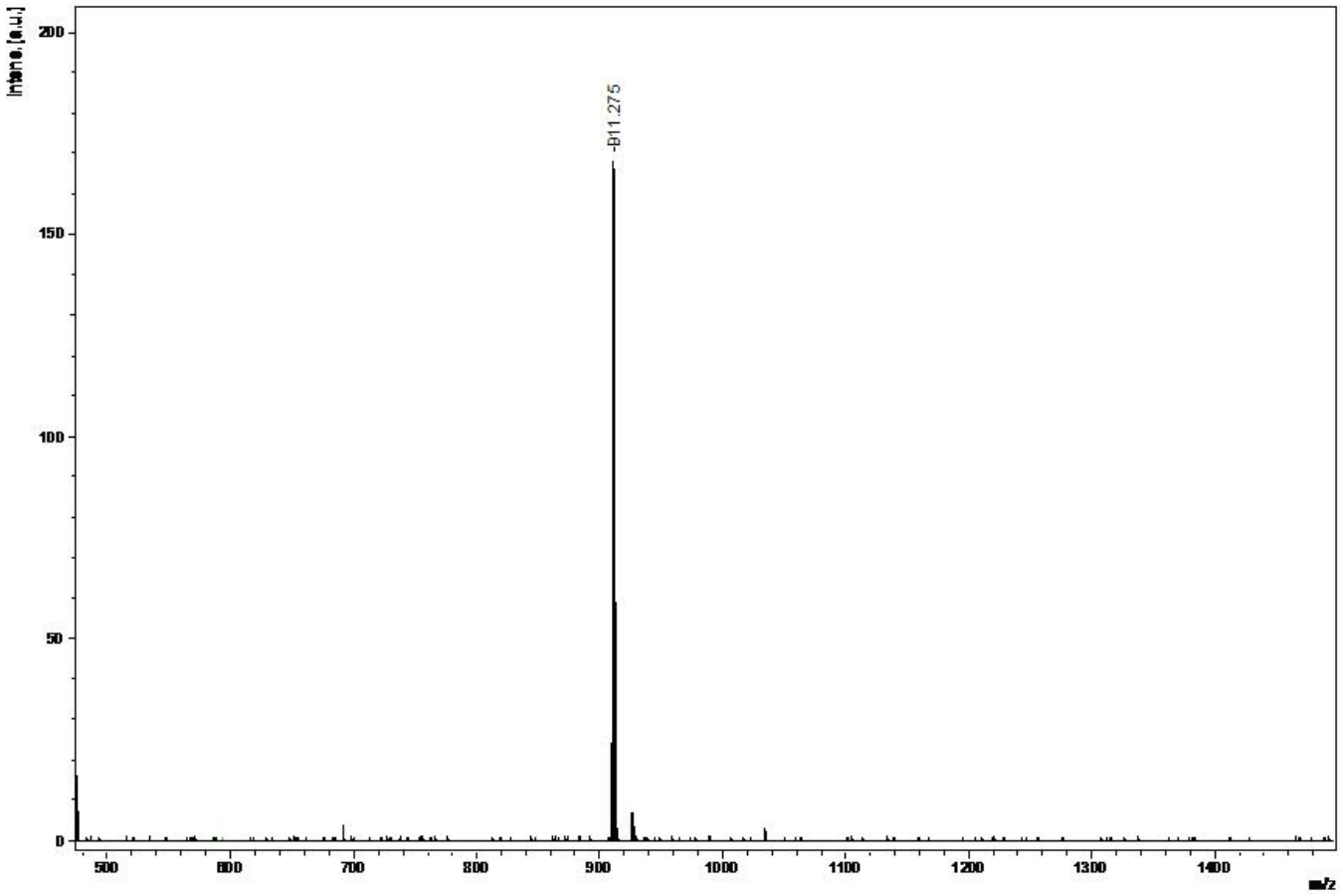


Figure S3. Negative (–) MALDI-TOF mass spectrum of **4**.

2.4

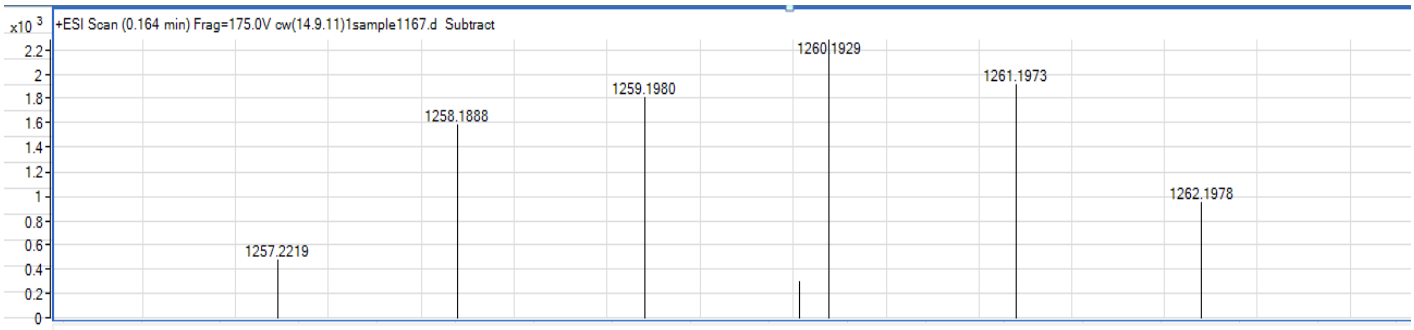


Figure S4. HR-ESI mass spectrum of **6**.

2.5

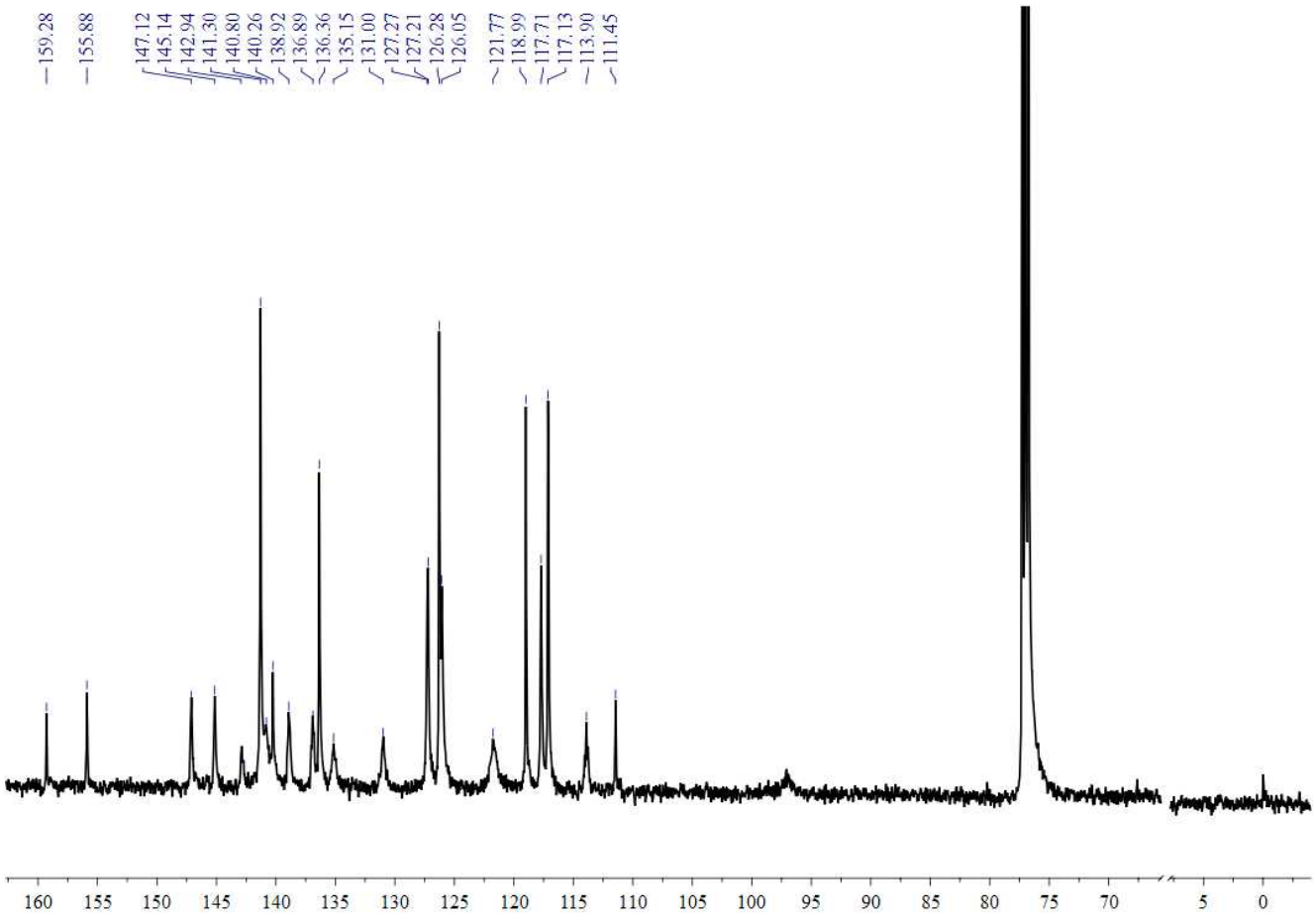


Figure S5. ^{13}C NMR spectrum of **4** (in $CDCl_3$, 298 K).

2.6

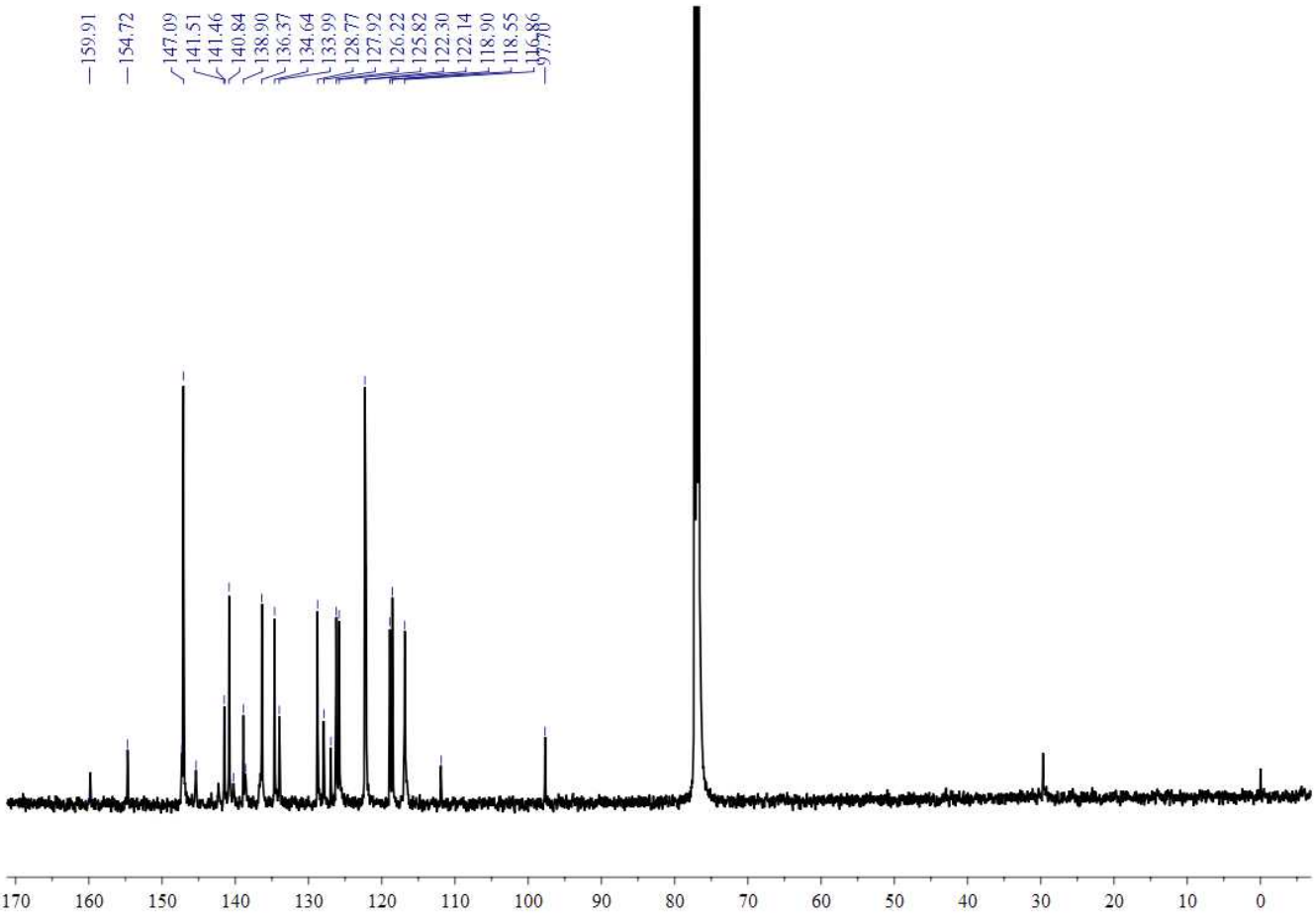


Figure S6. ^{13}C NMR spectrum of **6** (in $CDCl_3$, 298 K).

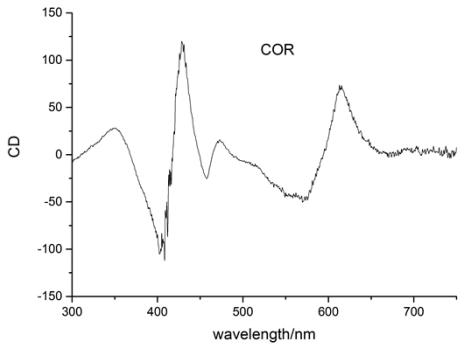
2.7

Table S1. Calculated TD-DFT spectra of the B3LYP optimized geometries of **4** and **6** calculated with the CAM-B3LYP functional and 6-31G(d) basis sets.

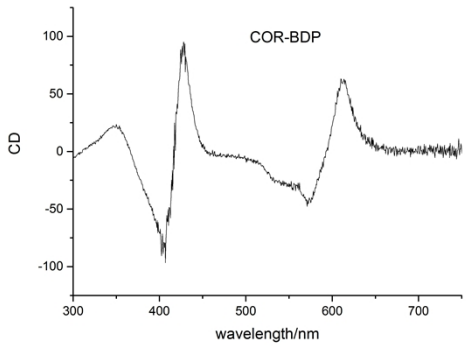
				4			
Band[a]	**#[b]**	**Calc[c]**			**Exp[d]**		**Wavefunction=[e]**
--	**1**	---	---	---	---	---	Ground state
Q	**2**	18.3	545	(0.12)	16.4	610	**36% a → -a; 33% s → -a; 19% s → -s; 9% a → -s;** …
Q	**3**	18.7	533	(0.16)	17.5	571	**44% s → -a; 29% a → -a; 14% s → -s; 12% a → -s;** …
BDY	**4**	26.5	377	(0.44)	21.9	456	94% BDY → BDY; …
B	**5**	27.6	361	(1.14)	23.4	428	**59% s→-s; 32% a → -a;** …
B	**6**	28.6	350	(1.28)	24.7	405	**68% a →s; 20% s → -a;** 5% H–3 → -a; …
				6			
Band[a]	**#[b]**	**Calc[c]**			**Exp[d]**		**Wavefunction=[e]**
--	**1**	---	---	---	---	---	Ground state
Q	**2**	18.8	532	(0.16)	16.1	620	**79% s → -a; 17% a → -s;** …
Q	**3**	18.9	528	(0.04)	16.9	590	**75% a → -a; 18% s → -s;** …
B	**7**	26.1	384	(0.13)	23.7	422	**38% a → -s;** 21% BDY →BDY; 11% a →BDY; 9% d_{π} → -a; 9% d_{π} → -s; **6% s → -a;** …
BDY	**8**	26.2	382	(0.59)	22.0	455	72% BDY →BDY; **9% a →-s**; 7% a →BDY; …
B	**10**	27.6	363	(0.62)	24.6	407	34% d_{π} → -a; **28% s →-s; 16% a →-a;** s → L+4; …

a − Band assignment described in the text. b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation. c − Calculated band energies (10^3.cm^{-1}), wavelengths (nm) and oscillator strengths in parentheses (f). d − Observed energies (10^3.cm^{-1}) and wavelengths (nm) in Figures 2 and 5. e − The wave functions based on the eigenvectors predicted by TD-DFT. One-electron transitions associated with Michl's perimeter model[3] are highlighted in bold. H and L refer to the HOMO and LUMO, respectively.

2.8



3



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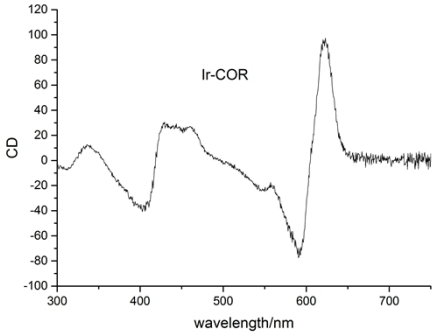

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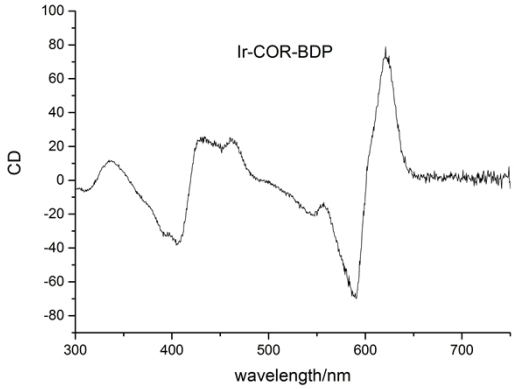

6

Figure S7. MCD spectra of **3, 4, 5** and **6** (in $CHCl_2$ 298 K).

2.9

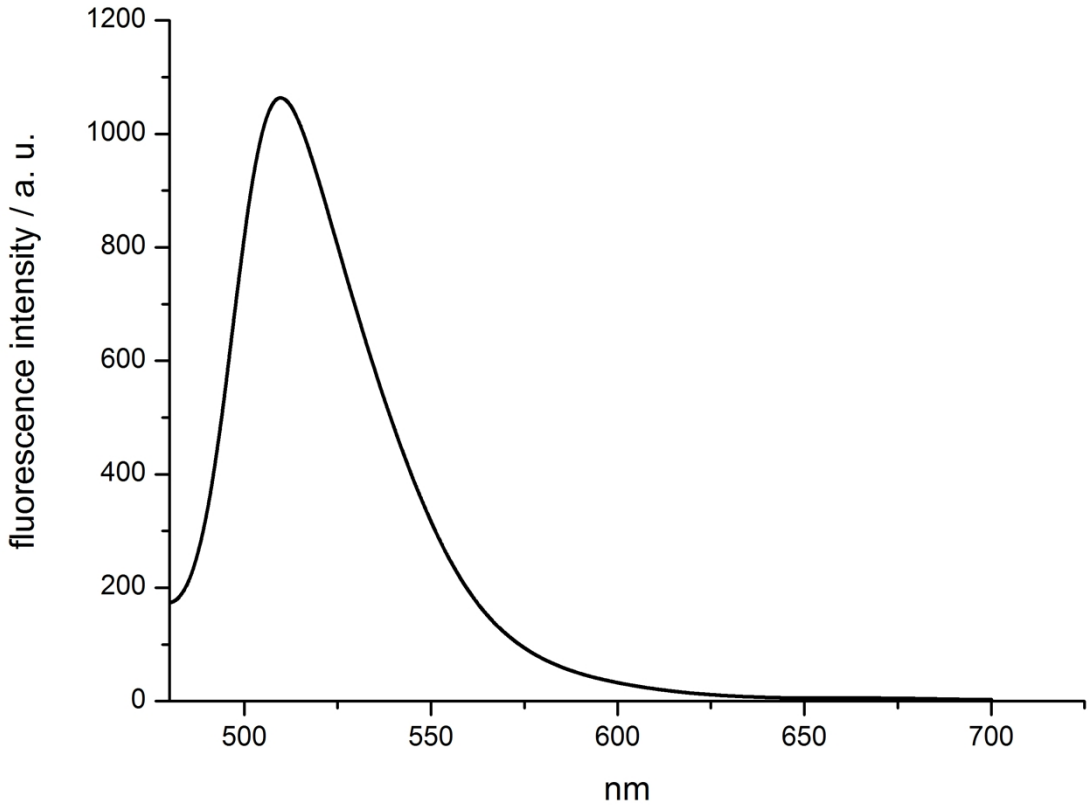

Figure S8. Fluorescence spectrum of an equimolar mixture of **2** and **3** upon excitation at 460 nm (in toluene, 298 K).

Reference:

(1)(a) V. Leen, P. Yuan, L. Wang, N. Boens and W. Dehaen, *Org. Lett.*, 2012, **24**, 6150. (b) M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405.

(2) (a) J. H. Palmer, M. W. Day, A. D. Wilson, L. M. Henling, Z. Gross and H. B. Gray, *J. Am. Chem. Soc*., 2008,**130**, 7786. (b) J. H. Palmer, A. Mahammed, K. M. Lancaster, Z. Gross and H. B. Gray, *Inorg. Chem.*, 2009, **48**, 9308.

(3) J. Michl, *J. Am. Chem. Soc.* **1978**, *100*, 6801. (b) J. Michl, *J. Am. Chem. Soc.* **1978**, *100*, 6812. (c) J. Michl, *Pure Appl. Chem.* **1980**, *52*, 1549. (d) J. Michl, *Tetrahedron* **1984**, *40*, 3845.