Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Reversible, controllable white-light emission of dye systems by dynamic covalent furan moiety exchanges

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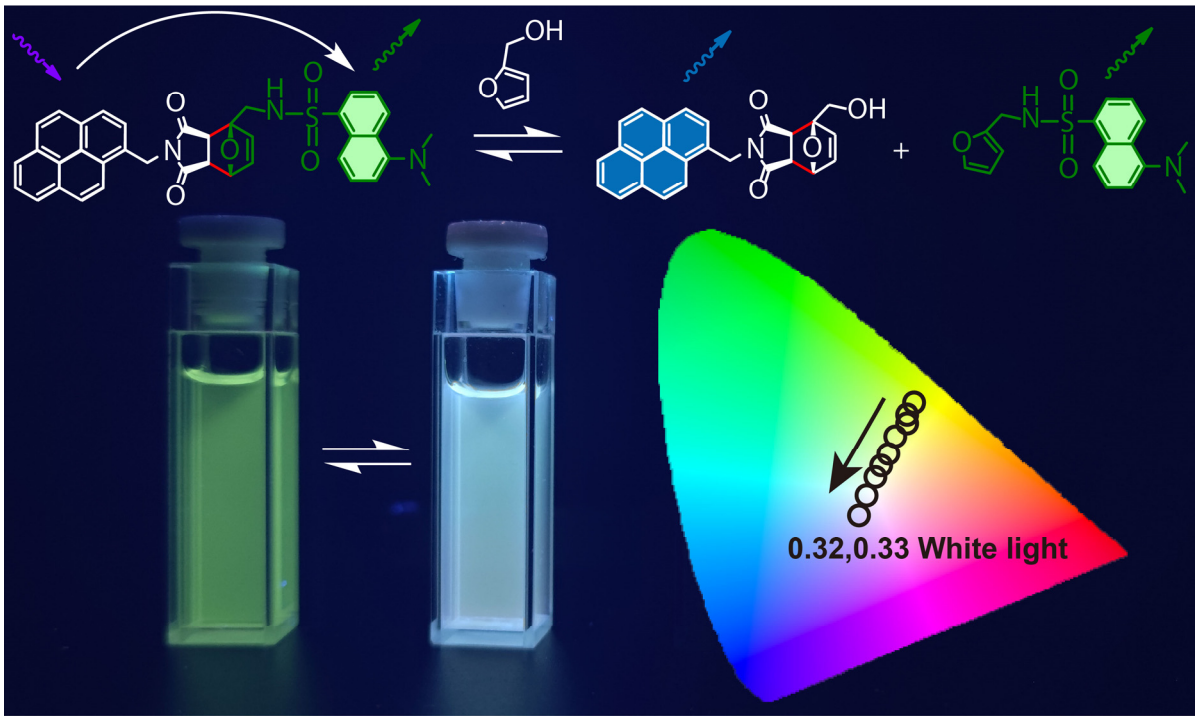


We demonstrate a new method to achieve white-light emission of dye systems from furan moiety exchanges by preventing interchromophore energy transfer.

Contents

1. Materials and methods

All commercially available reagents and solvents used in the experiment were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd and Shanghai Aladdin Biochemical Technology Co., Ltd, and the anhydrous solvent (dichloromethane) were prepared according to standard procedures. All solvents used for spectral measurements are spectrally pure and used without further purification. 300-400 mesh silica gel powder was used for column chromatography purification.

^{1}H NMR and ^{13}C NMR spectroscopy: NMR data were acquired on Bruker 400 MHz NMR spectrometer using CDCl3 as a solvent at room temperature. Tetramethylsilane (TMS) was used as internal standard.

High resolution mass spectrometer (HRMS): Mass spectra data were recorded on a miorOTOF-QII mass spectrometer using ESI. The tested samples were dissolved in methanol and tested at room temperature.

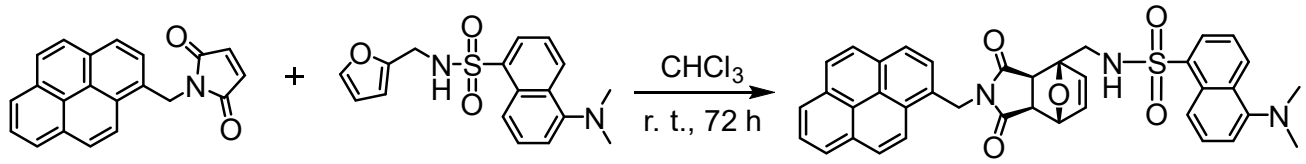
Infrared spectroscopy: Infrared spectra data were recorded on Bruker ALPHA II infrared spectrometer with KBr pellet at room temperature.

UV/Vis absorption spectroscopy: UV/Vis spectra data were measured by an Agilent Varian Cary 300 spectrometer equipped with quartz glass cuvettes and the extinction coefficients (ε) were calculated according to Lambert-Beer's law.

Fluorescence spectroscopy: The steady-state fluorescence emission spectra were measured using an Edinburgh FLS980 spectrofluorometer. Fluorescence decays were measured by using the time-correlated single-photon counting (TCSPC) technology,1 and nanosecond flash lamp as excitation light source, and the instrument response spectrum was measured by collecting the scattered excitation light of aqueous colloid silica.

Single crystal X-ray diffraction: Single crystal X-ray diffraction data were recorded on a Rigaku RAXIS RAPID IP diffractometer. X-ray crystals of exo-**2** and **3** were prepared by slow volatilization of their n-hexane / chloroform solution at ambient temperature.

2. Synthesis and characterization



5 **4** *exo*-**1**

Exo-**1**: Maleimide **5** (0.16 g，0.5 mmol) and **4** (0.17 g, 0.5 mmol) were mixed and added into chloroform (10 mL) with stirring at ambient temperature for 72 hours. And then the reaction mixture was purified by silica gel column chromatography using petroleum ether / DCM (3 / 40, *v* / *v*) as the eluent to obtain pure product as white solid (0.15 g, 50%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.55 (d, *J* = 8.0 Hz,1H; Ar*H*), 8.33 (m, 2H; Ar*H*), 8.24 (d, *J* = 8.0 Hz ,1H; Ar*H* in pyrene ring), 8.15 (m, 2H; Ar*H* in pyrene ring), 7.98 (m, 6H; Ar*H* in pyrene ring), 7.60 (t, *J* = 8.0 Hz,1H; Ar*H*), 7.50 (t, *J* = 8.0 Hz,1H; Ar*H*), 7.17 (d, *J* = 8.0 Hz,1H; Ar*H*), 6.47 (d, *J* = 8.0 Hz,1H; -C*H*=CH-), 6.39 (d, *J* = 4.0 Hz,1H; -CH=C*H*-), 5.89 (t, *J* = 8.0 Hz,1H; -N*H*-), 5.31 (m, 1H; -O-C*H*R_2), 5.21 (m, 2H; -CH_2-), 3.58, 3.29 (m, 2H; -NH-CH_2-), 2.92 (m, 2H; 2-C*H*R-), 2.86 (s, 6H; 2-CH_3).

^{13}C NMR ($CDCl_3$, ppm): δ = 175.70, 175.61, 152.12, 138.32, 136.83, 134.71, 131.27, 131.26, 130.79, 130.67, 130.01, 129.61, 129.60, 128.75, 128.74, 128.14, 127.98, 127.70, 127.39, 127.13, 126.12, 125.52, 125.40, 124.87, 124.74, 124.66, 123.32, 122.73, 118.70, 115.43, 90.26, 81.09, 50.18, 48.36, 45.50, 42.73, 40.80.

IR (KBr pellet, cm^{-1}): 3442.67, 3223.43, 2925.20, 2854.64, 1769.71, 1692.16, 1454.40, 1402.63, 1328.90, 1163.06, 1097.76, 1060.58, 971.51, 846.71, 785.62, 685.67.

HRMS (ESI): m/z calculated for $C_{38}H_{32}N_3O_5S$, $[M + H]^+$, 642.2057; found: 642.2057 $[M + H]^+$.

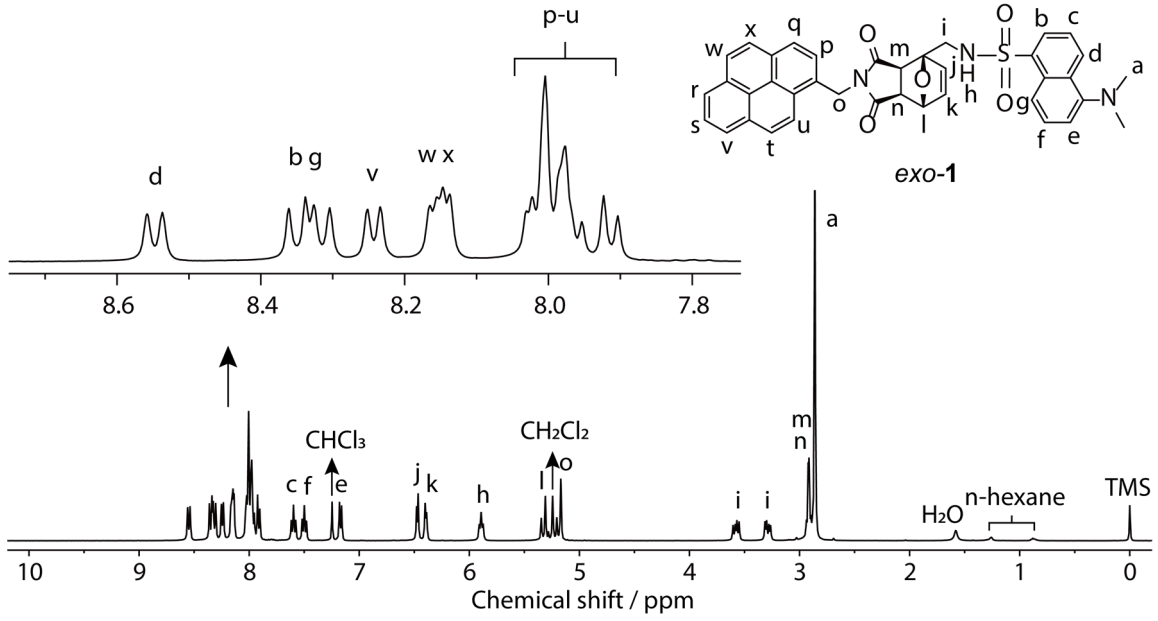


Fig. S1 ^{1}H NMR spectrum of *exo*-**1** in $CDCl_3$ and corresponding signal assignments.

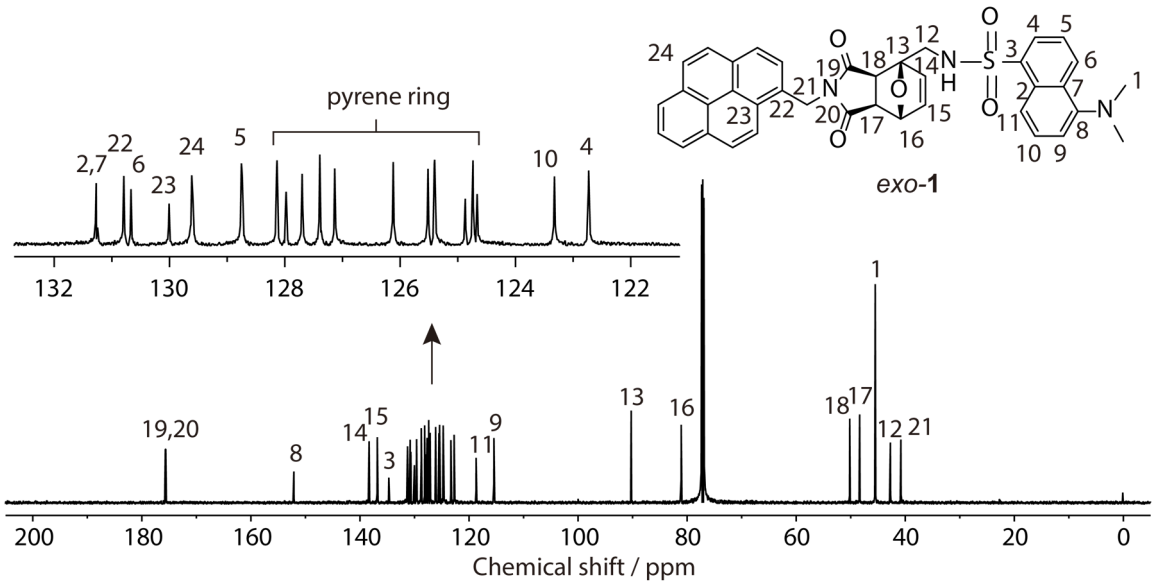


Fig. S2 ^{13}C NMR spectrum of *exo*-**1** in $CDCl_3$ with corresponding signal assignments.

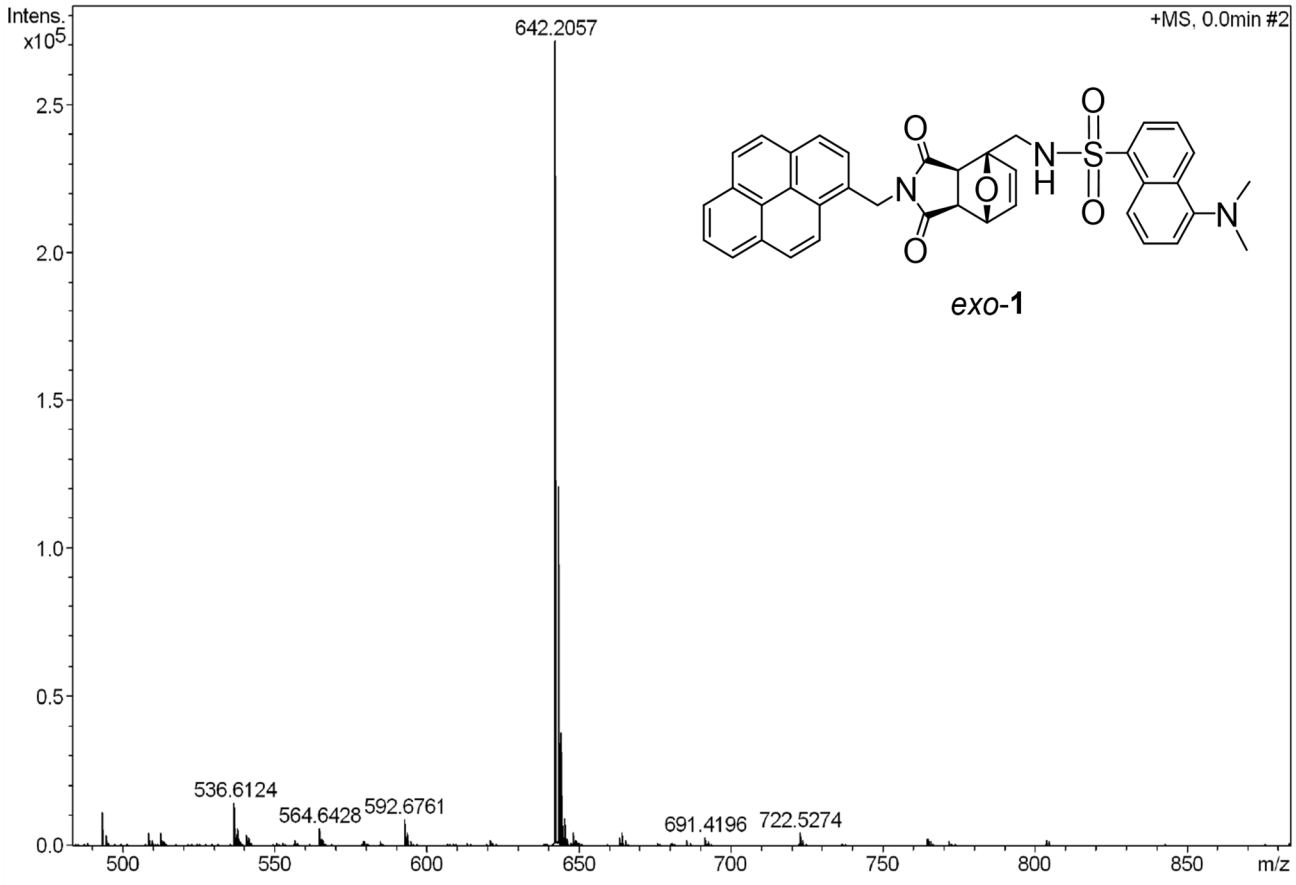
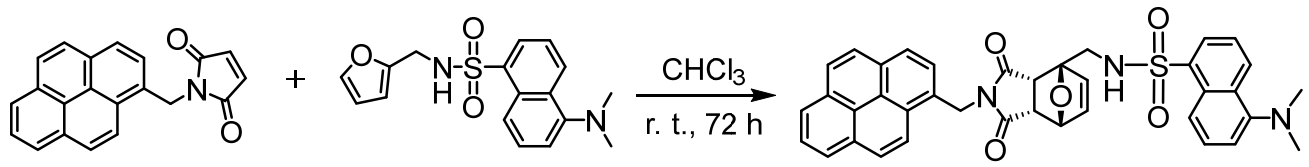


Fig. S3 High-resolution mass spectrum of *exo*-**1**.



5 **4** *endo*-**1**

Endo-**1**: Maleimide **5** (0.16 g，0.5 mmol) and **4** (0.17 g, 0.5 mmol) were mixed and added to chloroform (10 mL) with stirring at ambient temperature for 72 hours. And then the reaction mixture was purified by silica gel column chromatography using petroleum ether / DCM (3 / 40, *v* / *v*) as the eluent to give a white solid (0.04 g, 13%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.48 (m, 2H; Ar*H*), 8.30 (d, *J* = 4.0 Hz, 1H; Ar*H*), 8.25 (m, 3H; Ar*H* in pyrene ring), 8.19 (d, *J* = 4.0 Hz, 1H; Ar*H* in pyrene ring), 8.09 (m, 5H; Ar*H* in pyrene ring), 7.52 (t, *J* = 8.0 Hz, 1H; Ar*H*), 7.45 (t, *J* = 8.0 Hz, 1H; Ar*H*), 7.07 (d, *J* = 8.0 Hz, 1H; Ar*H*), 5.91 (d, *J* = 4.0 Hz, 1H; -C*H*=CH-), 5.72 (d, *J* = 8.0 Hz, 1H; -CH=C*H*-), 5.37 (t, *J* = 8.0 Hz, 1H; -N*H*-), 5.21 (s, 2H; -CH_2-), 5.12 (m, 1H; -O-C*H*R_2), 3.55 (m, 2H; -NH-CH_2-), 3.52 (m, 1H; -C*H*R-), 3.14 (d, *J* = 8.0 Hz, 1H; -C*H*R-), 2.84 (s, 6H; 2-CH_3).

^{13}C NMR ($CDCl_3$, ppm): δ = 174.66, 174.22, 151.99, 135.15, 134.67, 134.11, 131.40, 131.22, 130.70, 130.64, 130.06, 129.81, 129.48, 129.14, 128.99, 128.53, 128.13, 127.83, 127.36, 126.11, 125.51, 125.42, 124.78, 124.64, 124.49, 123.17, 118.52, 115.18, 89.79, 79.43, 47.99, 47.71, 45.36, 44.06, 40.50.

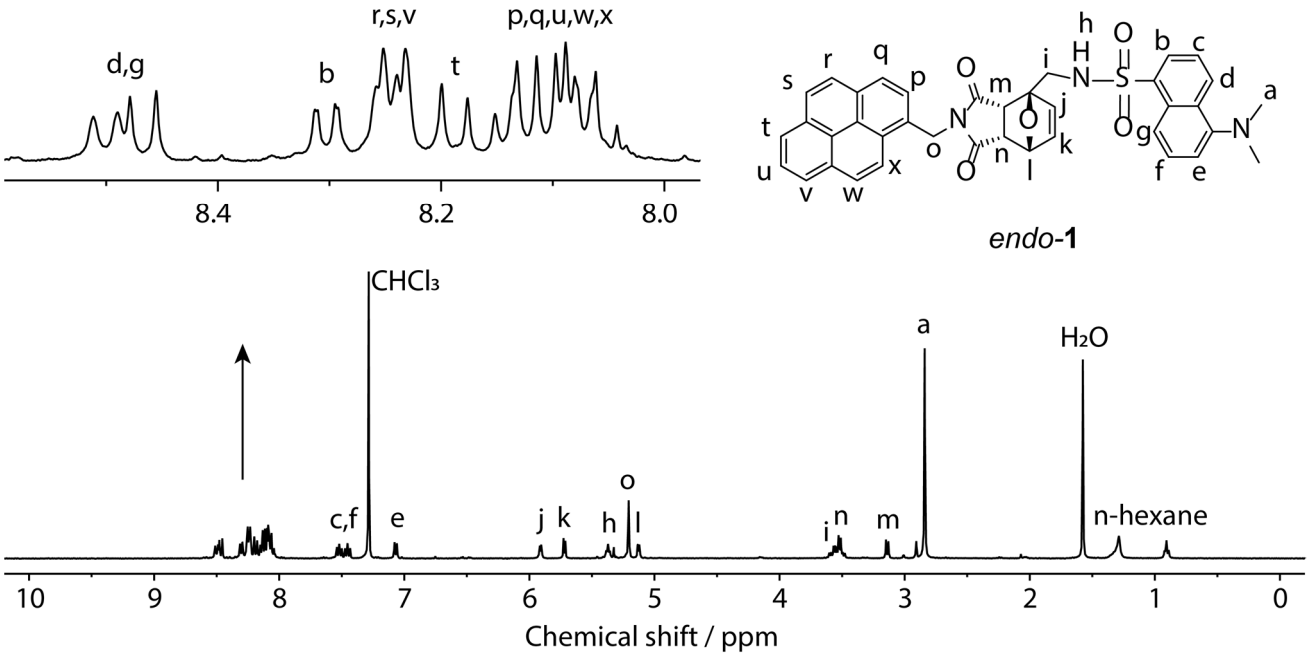


Fig. S4 ^{1}H NMR spectrum of *endo*-**1** in $CDCl_3$ and corresponding signal assignments.

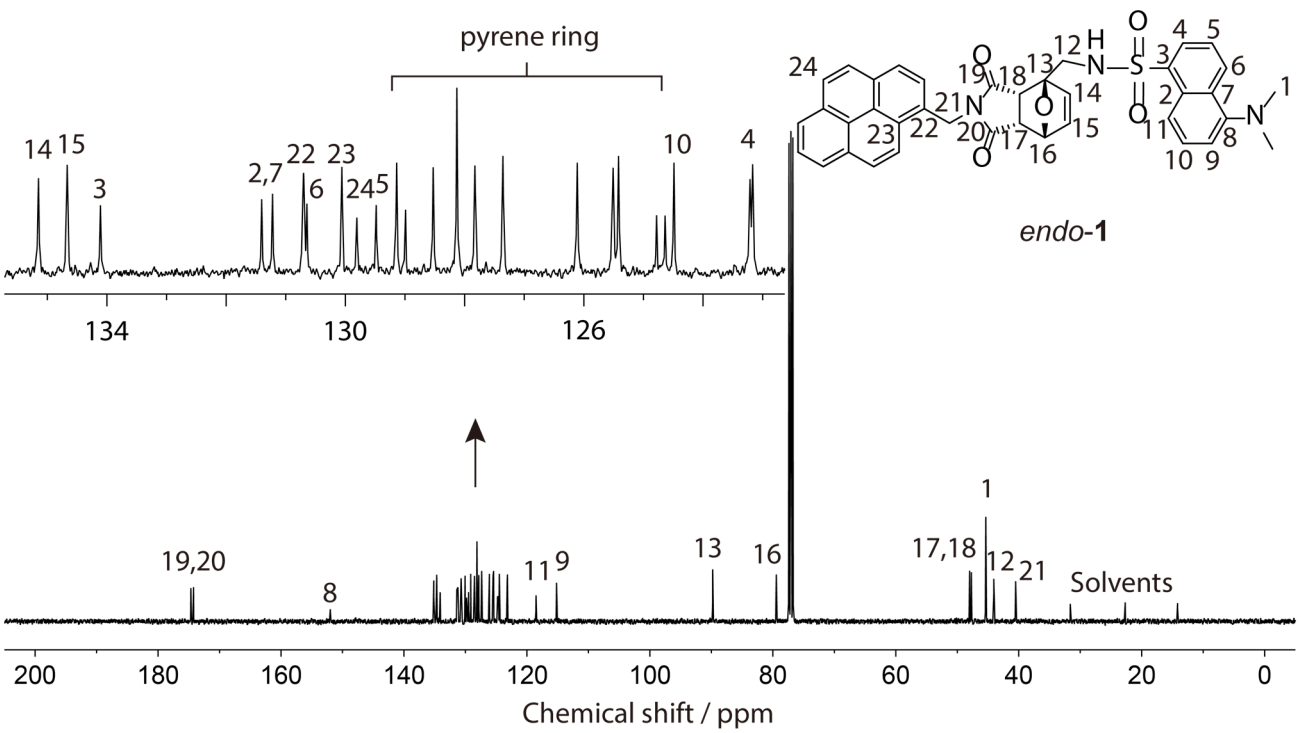
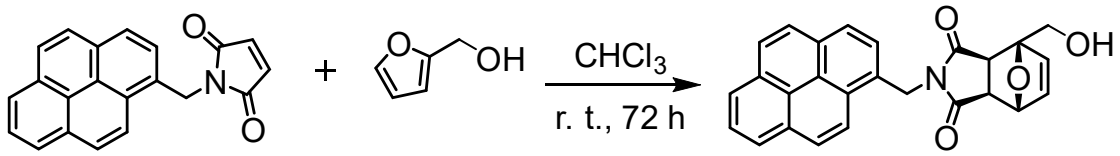


Fig. S5 ^{13}C NMR spectrum of *endo*-**1** in $CDCl_3$ with corresponding signal assignments.



5 *exo*-**2**

Exo-**2**: **5** (0.16 g, 0.5 mmol) and furfuryl alcohol (45 μL, 0.5 mmol) were dissolved in a mixture of chloroform (10 mL) and stirred at ambient temperature for 72 h. After the reaction was completed, the reaction mixture was purified by silica gel column chromatography (dichloromethane / ethyl acetate = 15 / 1, v / v) to give white solid (0.12 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.47 (d, *J* = 8.0 Hz, 1H, ArH in pyrene ring), 8.18 (m, 3H, ArH in pyrene ring), 8.12 (d, *J* = 4.0 Hz, 1H, ArH in pyrene ring), 8.03 (m, 4H, ArH in pyrene ring), 6.58 (d, *J* = 4.0 Hz, 1H, -CR-C*H*=CH-), 6.51 (d, *J* = 4.0 Hz, 1H, -CH=C*H*-CH-), 5.41 (s, 1H, -O-CR*H*-), 5.38 (s, 2H, -CH_2-), 4.08 (s, 2H, -CH_2-), 2.99 (m, 2H, -CR*H*-), 2.76 (m, 1H, -O*H*).

^{13}C NMR ($CDCl_3$, ppm) δ = 175.05, 174.67, 150.03, 131.46, 131.24, 130.58, 129.44, 128.95, 128.46, 128.29, 128.09, 127.26, 126.29, 125.71, 125.52, 124.70, 124.45, 123.21, 80.36, 79.76, 58.38, 47.07, 45.91, 40.27.

IR (KBr pellet, cm^{-1}) 2925.08, 2854.25, 1697.06, 1438.91, 1394.02, 1336.02, 1300.07, 1175.73, 1141.42, 1029.46, 967.85, 877.03, 850.04, 753.41, 704.02, 640.91.

HRMS (ESI): m/z calculated for $C_{26}H_{19}NO_4$, $[M+Na]^+$: 432.1206, found: 432.1217.

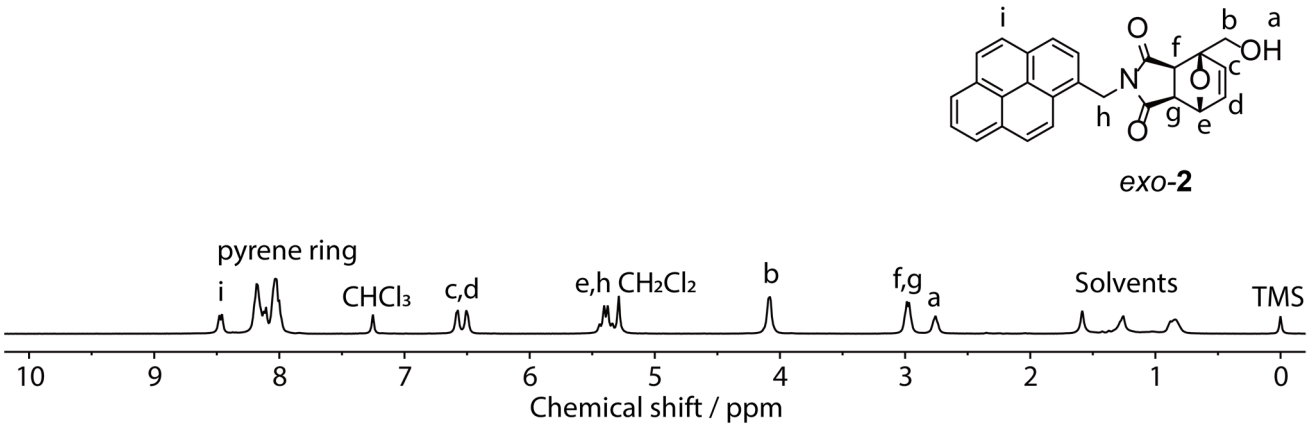


Fig. S6. ^{1}H NMR spectrum of *exo*-**2** in $CDCl_3$ and corresponding signal assignments.

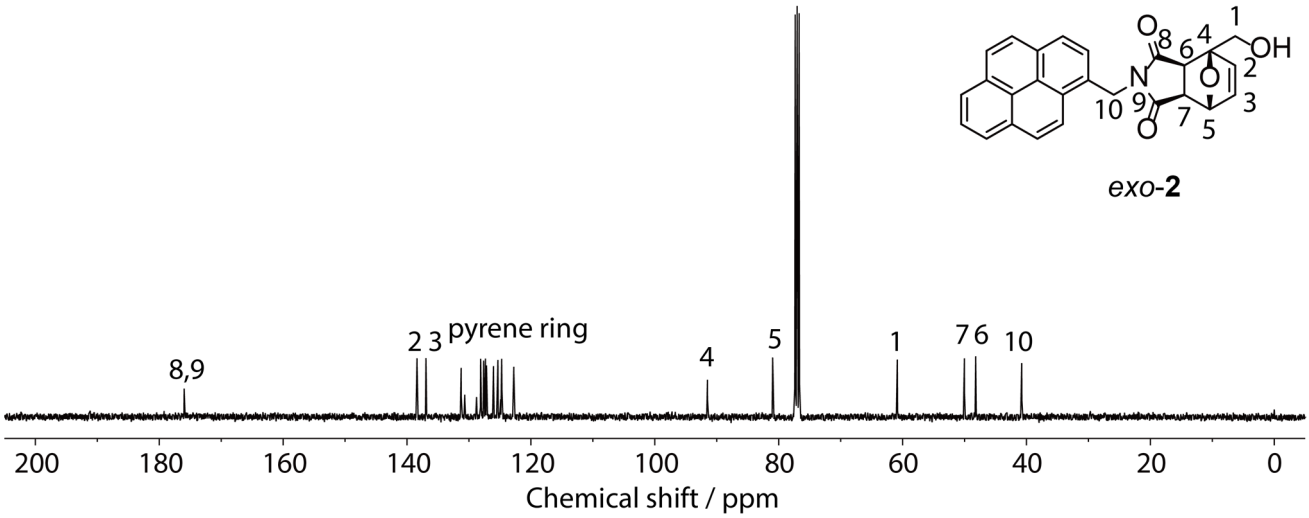
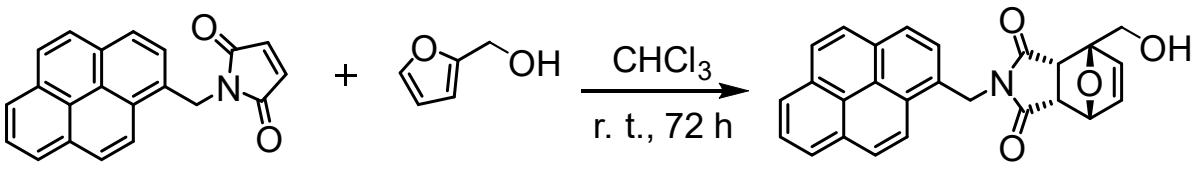


Fig. S7. ^{13}C NMR spectrum of *exo*-**2** in $CDCl_3$ and corresponding signal assignments.



5 *endo*-**2**

Endo-**2**: **5** (0.16 g, 0.5 mmol) and furfuryl alcohol (45 μL, 0.5 mmol) were dissolved in a mixture of chloroform (10 mL) and stirred at ambient temperature for 72 h. After the reaction was completed, the reaction mixture was purified by silica gel column chromatography (dichloromethane / ethyl acetate = 15 / 1, v / v) to give white solid (0.05 g, 27%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.52 (d, *J* = 8.0 Hz, 1H, ArH in pyrene ring), 8.14 (m, 8H, ArH in pyrene ring), 6.06 (d, *J* = 4.0 Hz, 1H, -CR-C*H*=CH-), 5.97 (d, *J* = 8.0 Hz, 1H, -CH=C*H*-CH-), 5.27 (s, 1H, -O-CR*H*-), 5.26 (s, 2H, -CH_2-), 4.20 (m, 2H, -CH_2-), 3.67 (m, 1H, -CR*H*-), 3.44 (d, *J* = 8.0 Hz, 1H, -CR*H*-), 1.96 (t, *J* = 8.0 Hz, 1H, -O*H*).

^{13}C NMR ($CDCl_3$, ppm) δ = 175.14, 174.66, 135.39, 134.55, 131.39, 131.22, 130.64, 129.16, 129.03, 128.28, 128.07, 127.80, 127.34, 126.08, 125.49, 125.37, 124.79, 124.64, 124.47, 123.25, 92.10, 79.61, 61.52, 48.02, 46.12, 40.47.

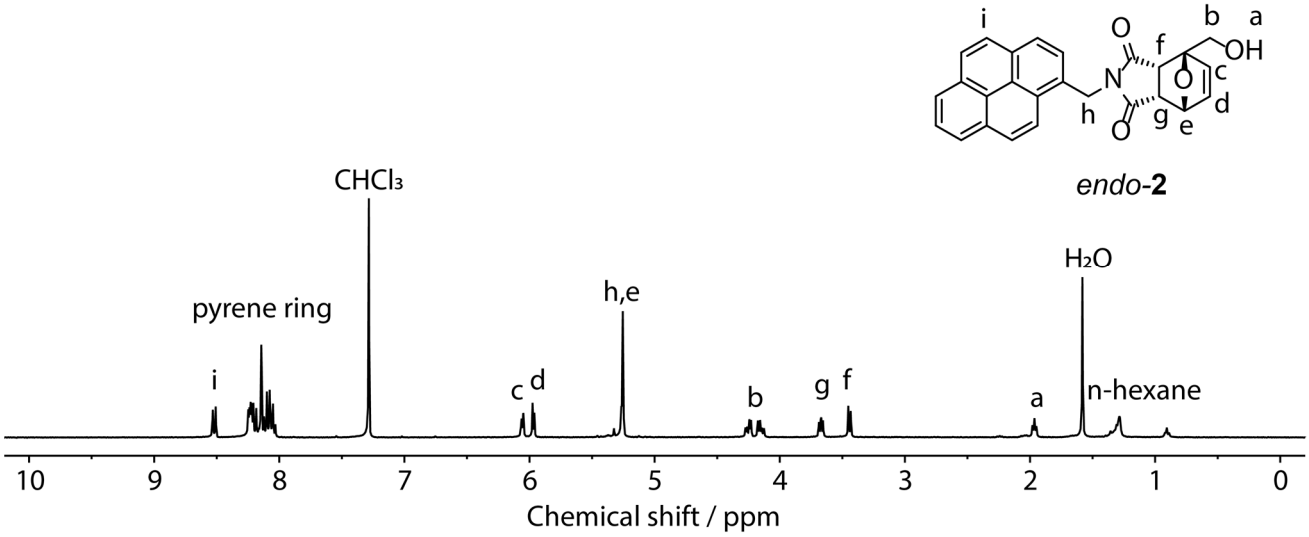


Fig. S8. ^{1}H NMR spectrum of *endo*-**2** in $CDCl_3$ and corresponding signal assignments.

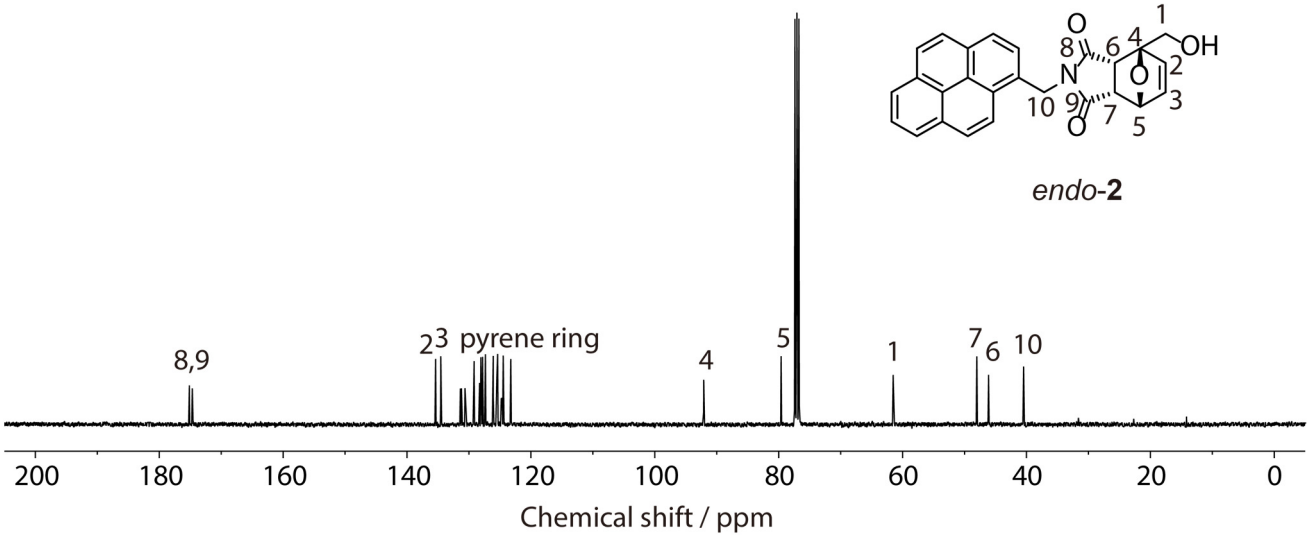
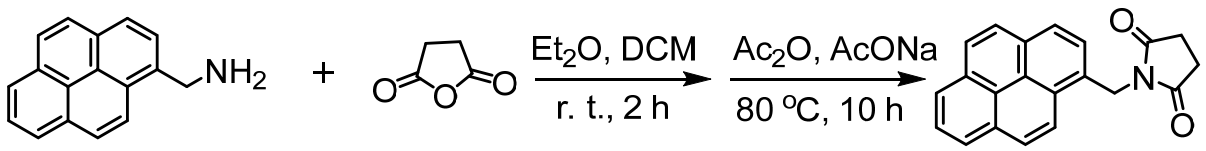


Fig. S9 ^{13}C NMR spectrum of *endo*-**2** in $CDCl_3$ with corresponding signal assignments.



3

N-(1-methylpyrene) succinimide (**3**): Triethylamine (0.12 g, 1.2 mmol) was added dropwise to the chloroform solution (10 mL) of 1-pyrenemethylamine hydrochloride (0.27 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 1 hour. After evaporation to remove the solvent, a white solid was obtained as crude product (1-pyrenemethylamine), which was directly used for the next step without further purification. The crude product of 1-pyrenemethylamine (0.44 g) was dissolved in DCM solution (5 mL) and then was added

dropwise to a diethyl ether solution (5 mL) of succinic anhydride (0.22 g, 2.25 mmol) with vigorous stirring at room temperature for 2 hours. After the reaction was completed, a white solid was given by filtration. The above dried white solid was subsequently added to acetic anhydride (2.2 mL) and then reaction mixture was heated to 80 °C with stirring for 10 hours in the presence of sodium acetate (0.21 g) as catalyst. After cooling to room temperature, the mixture was poured slowly into ice water with stirring rapidly and the precipitate was collected by filtration and drying. The crude product was further purified by silica gel column chromatography with petroleum ether / DCM (2 / 1, *v* / *v*) as the eluent to give a white solid (0.29 g, 49%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.60 (d, *J* = 8.0 Hz, 1H; Ar*H*), 8.17 (m, 4H; Ar*H*), 8.11 (d, *J* = 8.0 Hz, 1H; Ar*H*), 8.01 (m, 3H; Ar*H*), 5.38 (s, 4H; -C*H*$_2$-C*H*$_2$-), 2.68 (s, 2H; -C*H*$_2$-).

^{13}C NMR ($CDCl_3$, ppm): δ = 177.12, 131.34, 131.22, 129.10, 128.68, 128.63, 128.15, 127.69, 127.34, 126.03, 125.39, 125.30, 124.84, 124.62, 123.21, 40.47, 28.22.

IR (KBr pellet, cm^{-1}): 3446.53, 3043.52, 2977.10, 2937.56, 1770.60, 1698.11, 1602.25, 1443.44, 1404.13, 1345.83, 1326.61, 1296.61, 1248.41, 1162.89, 1099.40, 1063.13, 1004.93, 909.47, 842.81, 816.49, 766.46, 705.96, 666.98, 639.44.

HRMS (ESI): m/z calculated for $C_{21}H_{16}NO_2$ $[M + H]^+$, 314.1176; found: 314.1175 $[M + H]^+$.

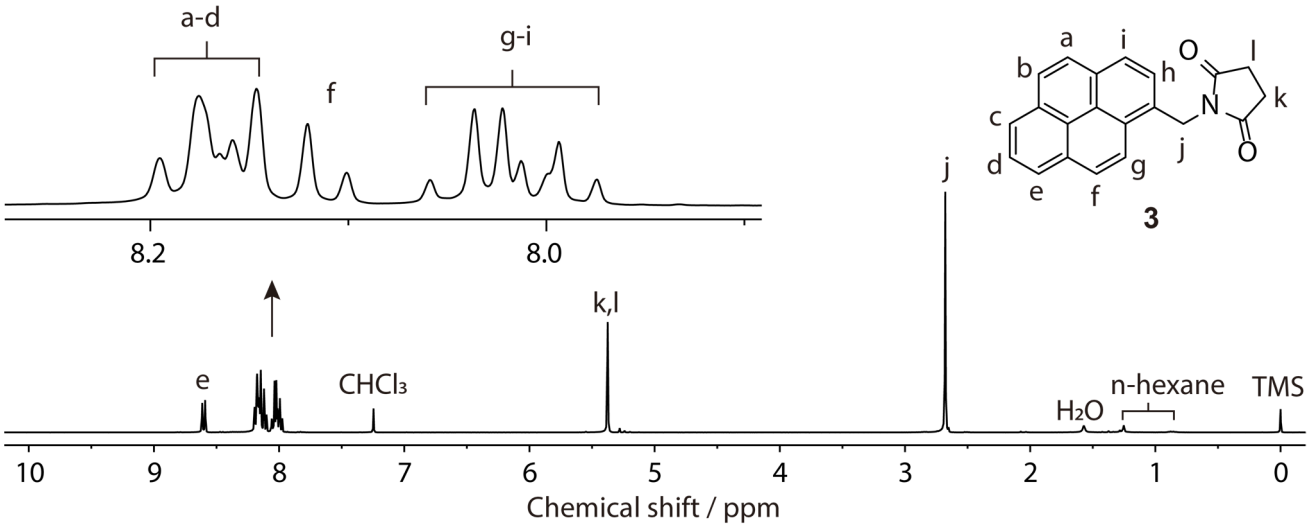


Fig. S10 ^{1}H NMR spectrum of **3** in $CDCl_3$ and corresponding signal assignments.

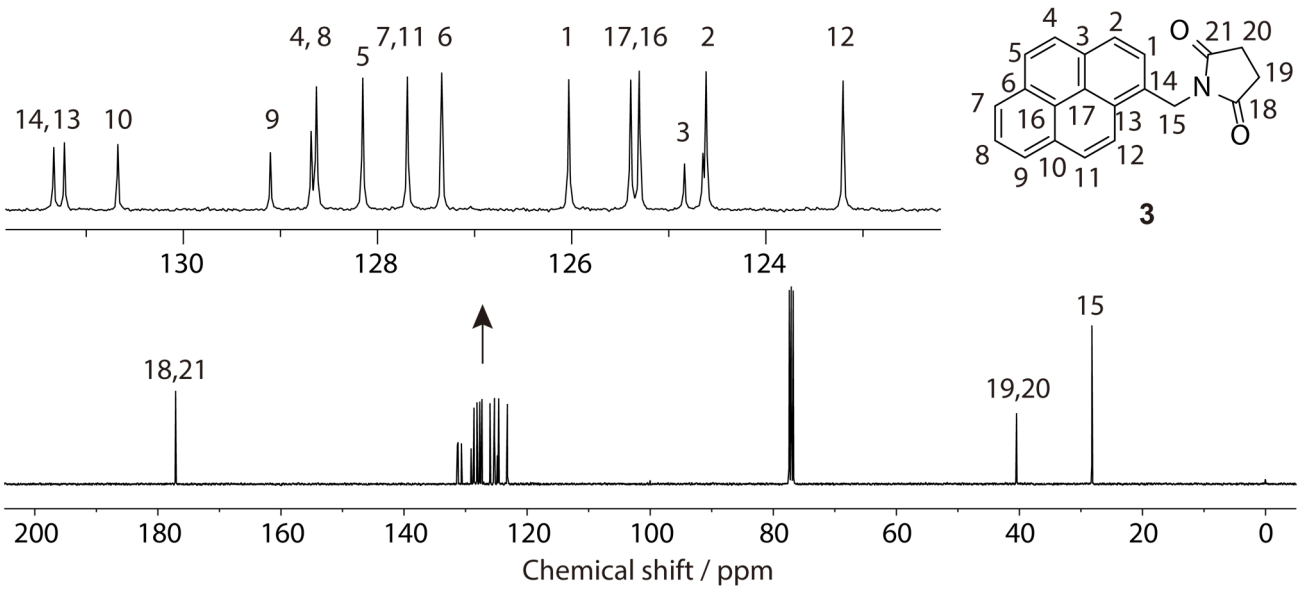
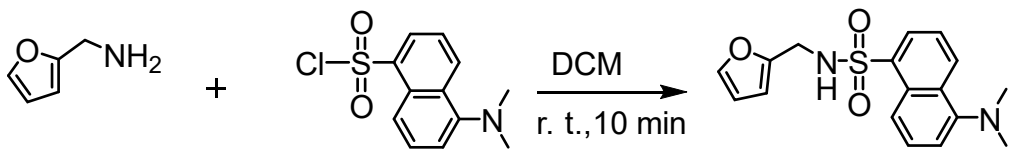


Fig. S11 ^{13}C NMR spectrum of **3** in $CDCl_3$ and corresponding signal assignments.



Acceptor **4**: Dansyl chloride (0.27g, 1.0 mmol) in dry dichloromethane (DCM) was added dropwise to the dry DCM (10 mL) solution of 2-furanmethanamine (0.12 g, 1.2 mmol) under an inert Ar atmosphere. The reaction mixture was stirred vigorously for 10 minutes at ambient temperature. The solvent was removed. The crude product was purified by silica gel column chromatography using ethyl acetate / petroleum ether (1 / 4, *v* / *v*) to give pure product as white solid (0.29 g, 92%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.50 (d, *J* = 8.5 Hz, 1H; Ar*H*), 8.23 (m, *J* = 11.2, 8.0 Hz, 2H; Ar*H*), 7.50 (m, *J* = 20.6, 8.0 Hz, 2H; Ar*H*), 7.16 (d, *J* = 7.5 Hz, 1H; Ar*H*), 7.01 (s, 1H; -O-C*H*=CH-), 6.02 (d, *J* = 2.6 Hz, 1H; -O-CH=C*H*-), 5.87 (d, *J* = 3.0 Hz, 1H; -C*H*=CR_2), 5.16 (t, *J* = 6.0 Hz, 1H; -SO_2-N*H*-), 4.12 (d, *J* = 6.1 Hz, 2H; -CH_2-), 2.87 (s, 6H; 2-CH_3).

^{13}C NMR ($CDCl_3$, ppm): δ = 151.96, 149.42, 142.20, 134.76, 130.49, 129.58, 128.40, 123.11, 118.63, 115.14, 110.13, 107.96, 45.41, 40.20.

IR (KBr pellet, cm^{-1}): 3052.99, 2849.73, 1567.94, 1459.33, 1406.91, 1295.80, 1225.08, 1199.00, 1142.96, 1035.54, 917.92, 786.94, 756.41.

HRMS (ESI): m/z calculated for $C_{17}H_{19}N_2O_3S$, $[M + H]^+$, 331.1111; found: 331.1108 $[M + H]^+$.

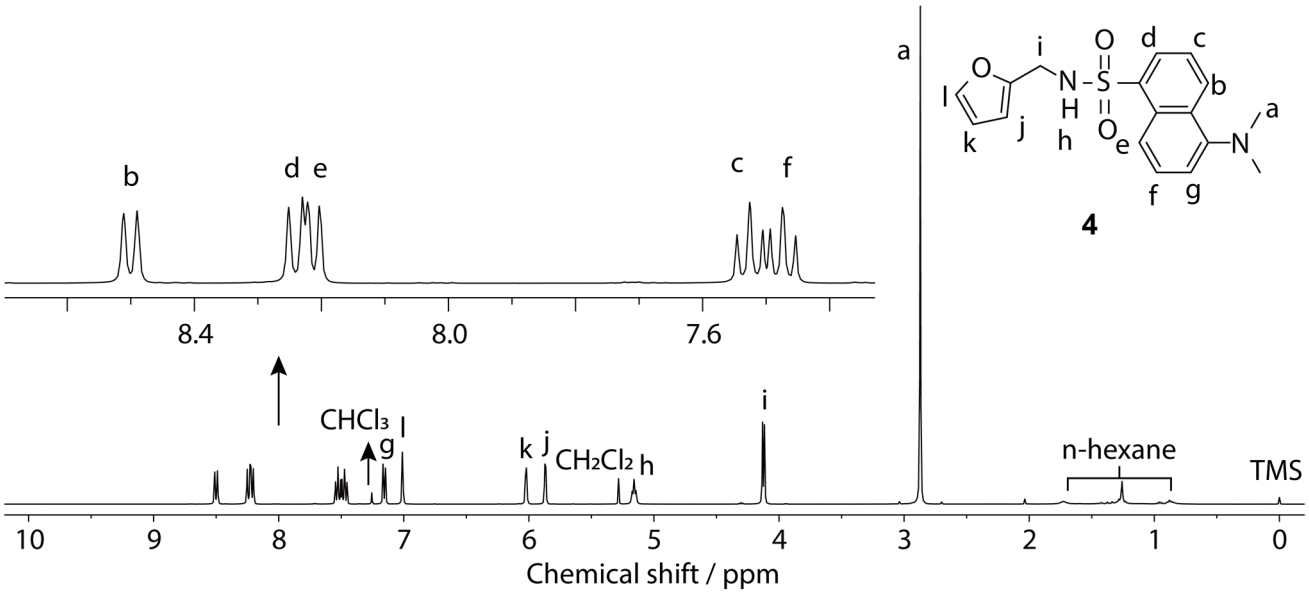


Fig. S12 ^{1}H NMR spectrum of **4** in $CDCl_3$ and corresponding signal assignments.

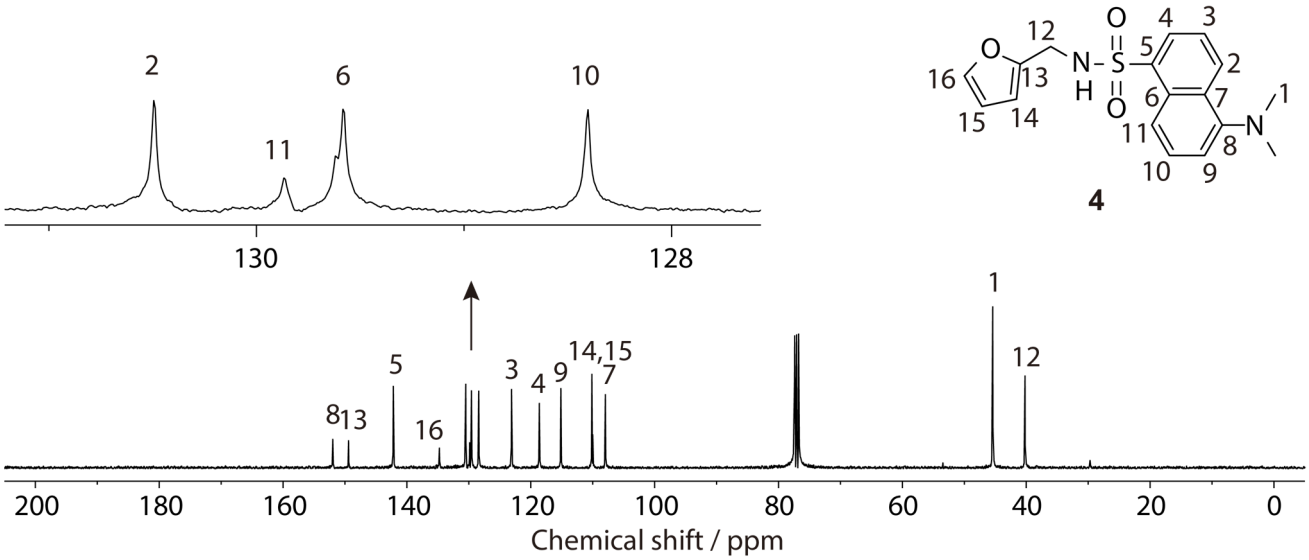
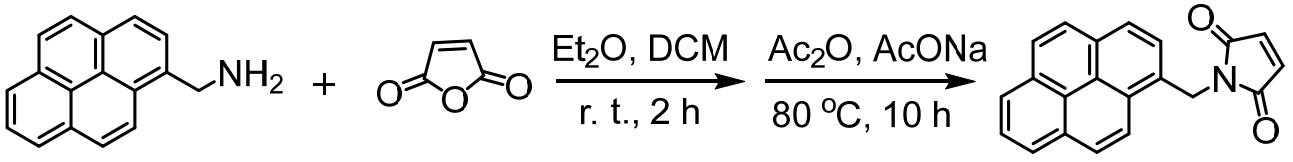


Fig. S13 ^{13}C NMR spectrum of **4** in $CDCl_3$ and corresponding signal assignments.



5

N-(1-methylpyrene) maleimide (**5**): Triethylamine (0.12 g, 1.2 mmol) was added dropwise to the chloroform solution (10 mL) of 1-pyrenemethylamine hydrochloride (0.27 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 1 hour. After evaporation to remove the solvent, a white solid was obtained as crude product (1-pyrenemethylamine), which was directly used for the next step without further purification. The crude product of 1-pyrenemethylamine (0.44 g) was dissolved in DCM solution (5 mL) and then was added

dropwise to a diethyl ether solution (5 mL) of maleic anhydride (0.22 g, 2.25 mmol) with vigorous stirring at room temperature for 2 hours. After the reaction was completed, a yellow solid was obtained by filtration. The above dried yellow solid was subsequently added to acetic anhydride (2.2 mL) and then reaction mixture was heated to 80 °C with stirring for 10 hours in the presence of sodium acetate (0.21 g) as catalyst. After cooling to room temperature, the mixture was poured slowly into ice water with stirring rapidly and the precipitate was collected by filtration and drying. The crude product was further purified by silica gel column chromatography with petroleum ether / DCM (2 / 1, *v* / *v*) as the eluent to give a yellow solid (0.22 g, 38%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.53 (d, *J* = 8.0 Hz,1H; Ar*H*), 8.16 (m, 4H; Ar*H*), 8.09 (m, 1H; Ar*H*), 8.00 (m, 3H; Ar*H*), 6.66 (s, 2H; -C*H*=C*H*-), 5.38 (s, 2H; -CH_2-).

^{13}C NMR ($CDCl_3$, ppm): δ = 170.61, 134.24, 131.31, 131.25, 130.69, 129.04, 128.83, 128.17, 127.93, 127.66, 127.35, 126.03, 125.41, 125.32, 124.87, 124.69, 122.85, 39.58.

IR (KBr pellet, cm^{-1}): 3446.53, 3043.52, 2977.10, 2937.56, 1770.60, 1698.11, 1602.25, 1443.44, 1404.13, 1345.83, 1326.61, 1296.61, 1248.41, 1162.89, 1099.40, 1063.13, 1004.93, 909.47, 842.81, 816.49, 766.46, 705.96, 666.98, 639.44.

HRMS (ESI): m/z calculated for $C_{21}H_{13}NO_2Na$, $[M + Na]^+$, 334.0838; found: 334.0838 $[M+Na]^+$.

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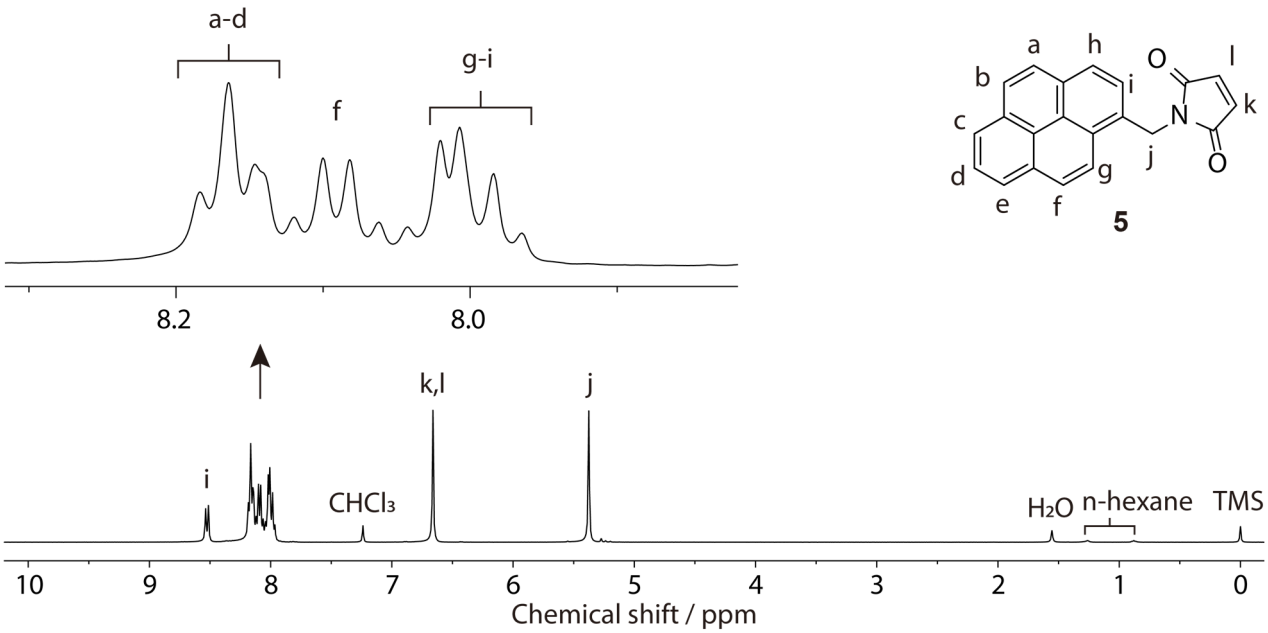

Fig. S14. ^{1}H NMR spectrum of maleimide **5** in $CDCl_3$ and corresponding signal assignments.

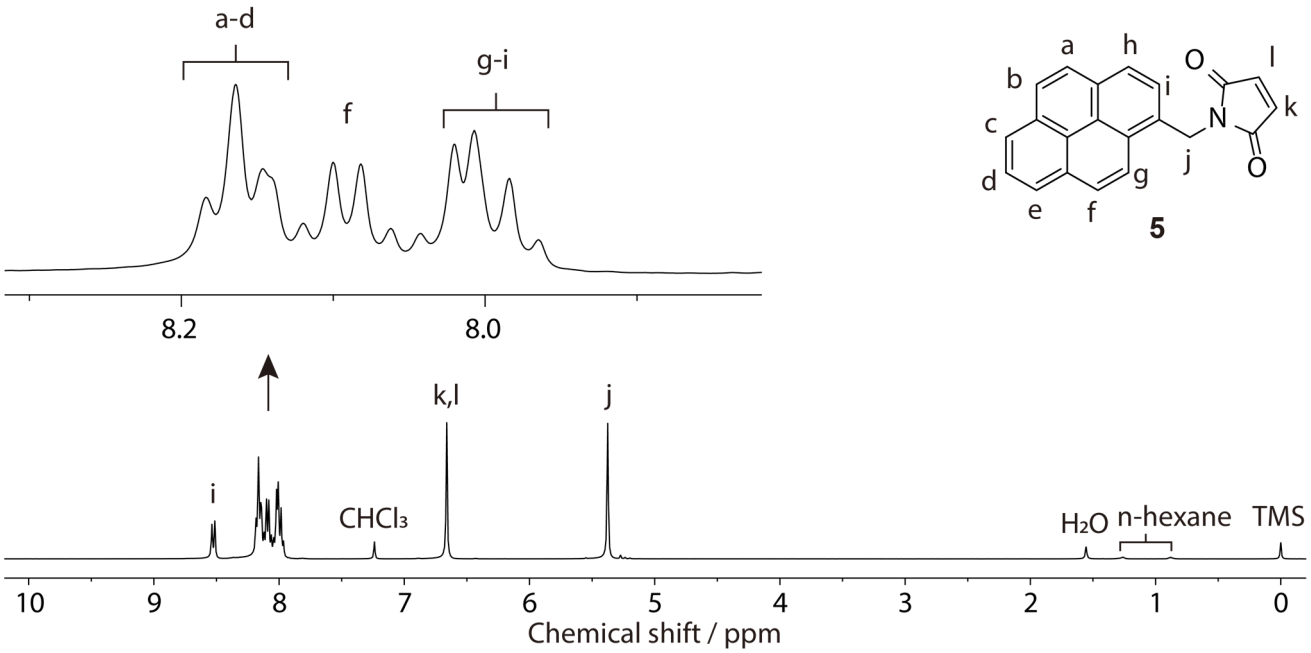

Fig. S15. ^{13}C NMR spectrum of maleimide **5** in $CDCl_3$ and corresponding signal assignments.

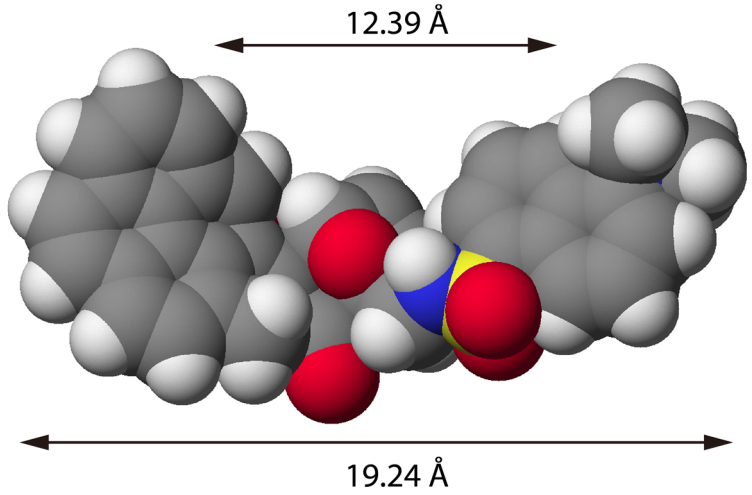

Fig. S16. Energy-optimized molecular structure of *exo*-**1** calculated by AM1 semi-empirical method.

3. Single-crystal X-ray diffraction

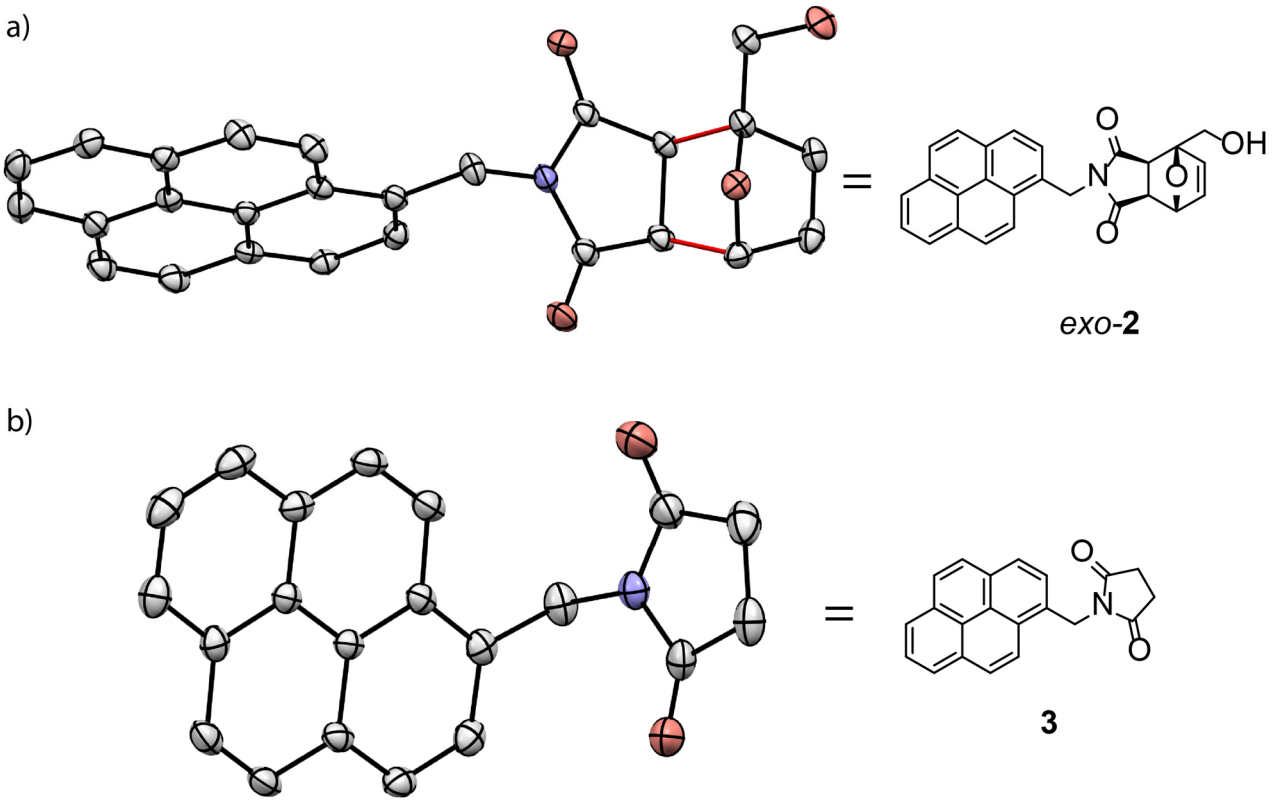

Fig. S17. Molecular structures (ORTEP) of *exo*-**2** (a), **3** (b) determined by single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50 % probability level. All hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for *exo*-**2** and **3**.

Identification code	*exo*-**2**	**3**
Empirical formula	$C_{26}H_{19}O_4N$	$C_{21}H_{15}O_2N$
Formula weight	409.42	313.34
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
Unit cell dimensions	a = 8.2348(3) Å, b = 9.0936(4) Å, c = 12.7865(4) Å $\alpha = 90^0$, $\beta = 94.996(3)^0$, $\gamma = 90^0$	a = 4.6945(2) Å, b = 9.6477(3) Å, c = 33.0272(9) Å $\alpha = 90^0$, $\beta = 90^0$, $\gamma = 90^0$
Volume	953.87(6) $Å^3$	1495.84(9) $Å^3$
Z	2	4
Calculated density	1.425 g / cm^3	1.391 g/cm^3
Wavelength	0.71073 Å	0.71073 Å
Temperature	113.15 K	113.15 K
Absorption coefficient	0.097 mm^{-1}	0.090 mm^{-1}
F(000)	428	656.0
Crystal size	0.25 x 0.2 x 0.17 mm	0.26 x 0.21 x 0.17mm
Theta range for data collection	4.966^0 to 52.738^0	4.398^0 to 64.596^0
Limiting indices	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$	$-6 \leq h \leq 6$, $-13 \leq k \leq 13$, $-47 \leq l \leq 44$
Reflections collected / unique	10240 / 3899 [R(int) = 0.0392]	16364 / 4918 [R(int) = 0.0443]
Completeness to theta = 26.369	1.87 / 1.00	1.59 / 0.93
Max. and min. transmission	1.000 and 0.758	1.000 and 0.711
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3899 / 2 / 292	4918 / 0 / 218
Goodness-of-fit on F^2	1.060	1.038
Largest diff. peak and hole	0.18 and -0.23 e. $Å^{-3}$	0.23 and -0.21 e. $Å^{-3}$
Final R indices [I>=2sigma(I)]	$R_1 = 0.0418$, $wR_2 = 0.1002$	$R_1 = 0.0489$, $wR_2 = 0.1178$
R indices (all data)	$R_1 = 0.0462$, $wR_2 = 0.1053$	$R_1 = 0.0584$, $wR_2 = 0.1269$

4. UV/Vis absorption and fluorescence spectroscopy

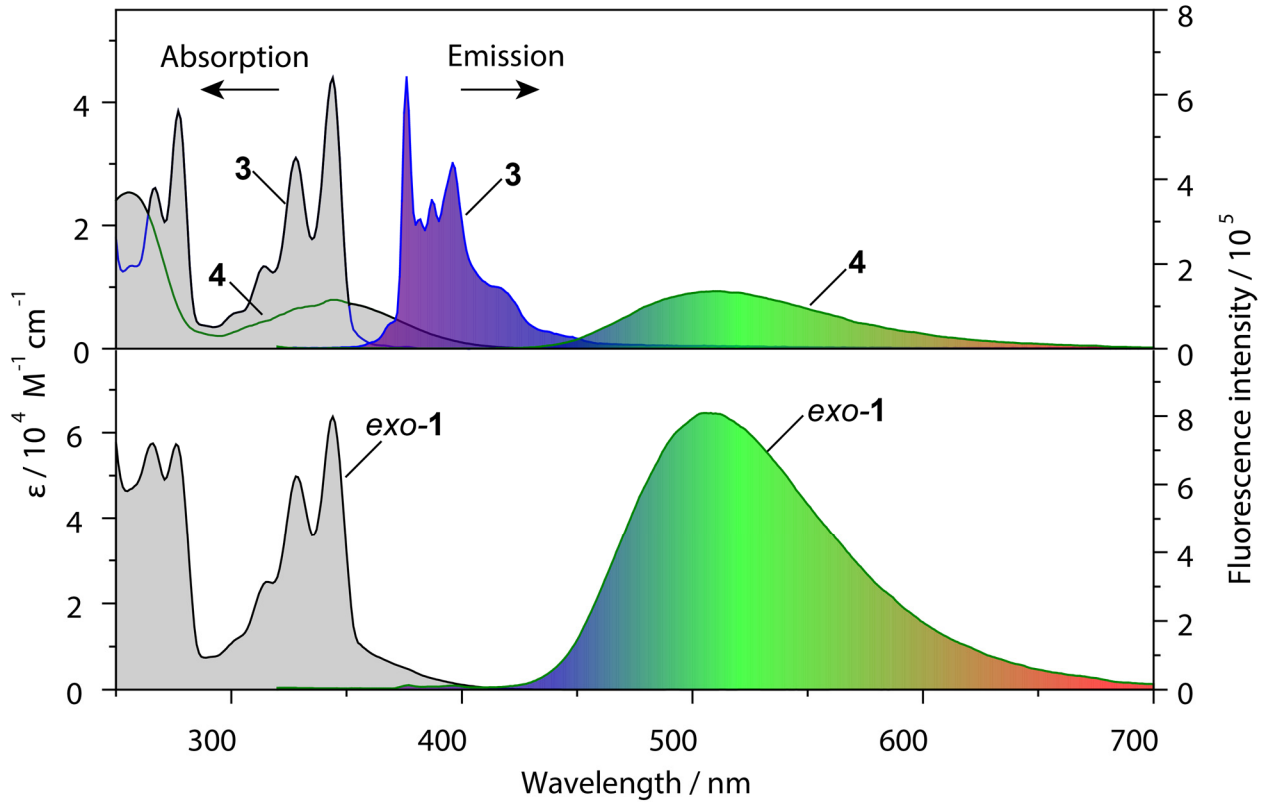

Fig. S18 UV/Vis absorption and fluorescence emission spectra of *exo*-**1**, **3** and **4** in dichloromethane, [*exo*-**1**] = [**3**] = [**4**] = 1.0 × 10^{-5} M, λ_{ex} = 315 nm.

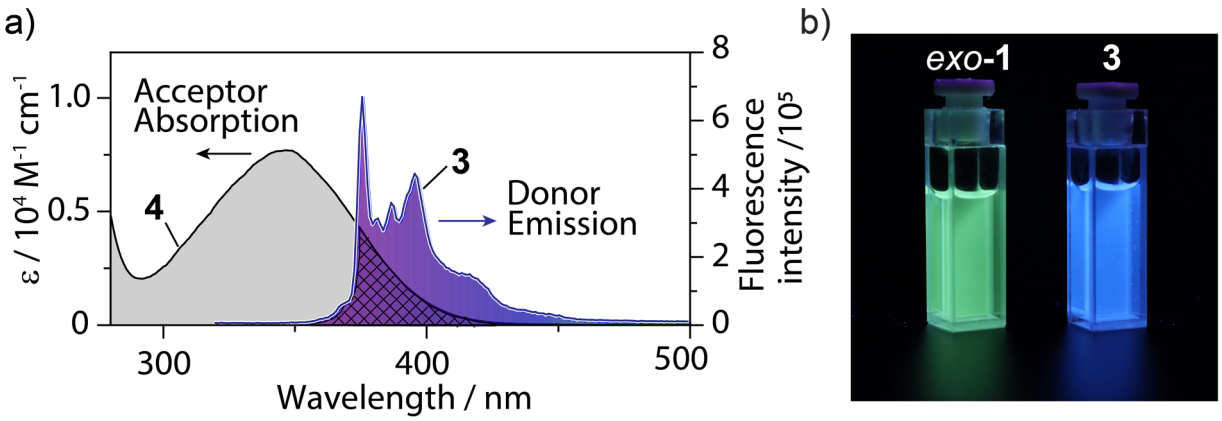

Fig. S19. a) Spectral overlap of donor **3** (emission) and acceptor **4** (absorption) in dichloromethane, [**3**] = [**4**] = 1.0 × 10^{-5} M. b) Photograph of *exo*-**1** and **3** in dichloromethane under 365 nm UV lamp, [*exo*-**1**] = 1.0 × 10^{-5} M, [**3**] = 1.0 × 10^{-4} M.

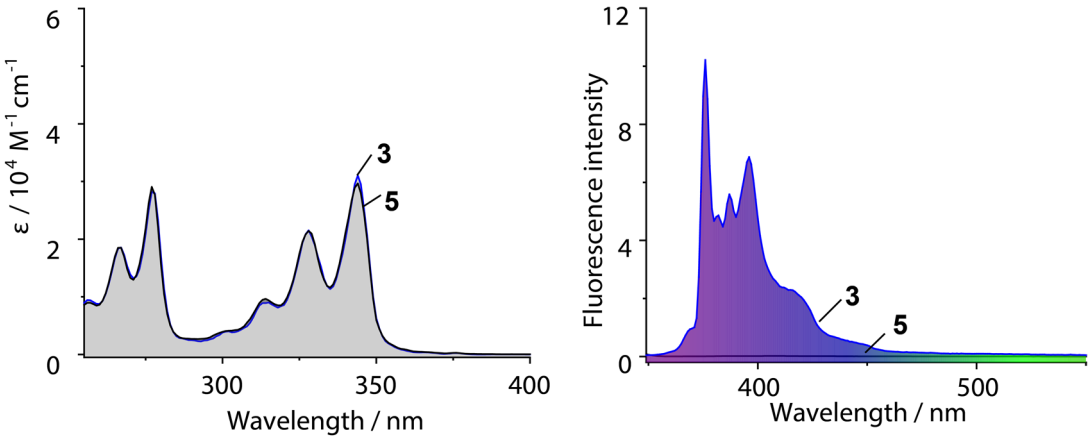

Fig. S20 UV/Vis absorption and fluorescence emission spectra of **3** and **5** in dichloromethane, [**3**] = [**5**] = 1.0 × 10^{-5} M, λ_{ex} = 340 nm.

5. Time-resolved fluorescence

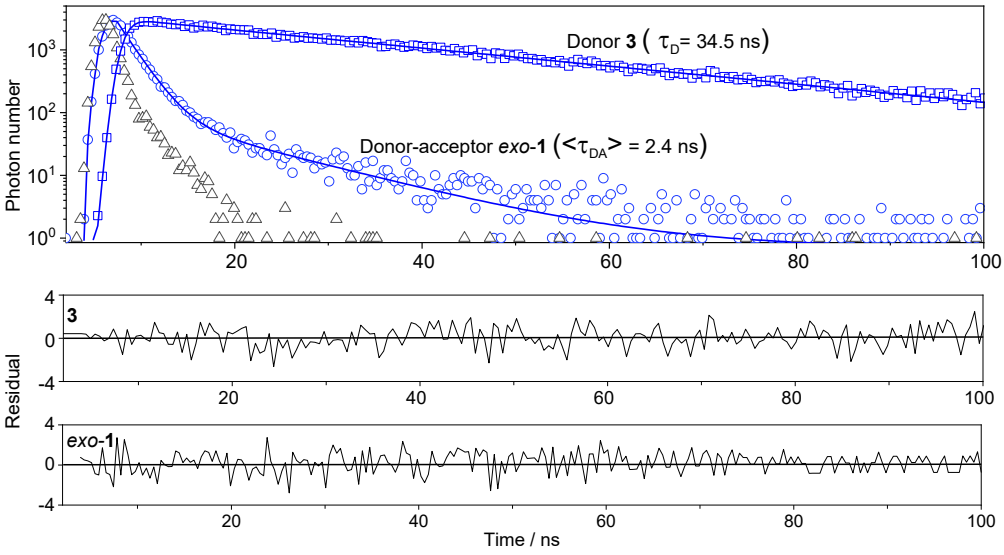

Fig. S21 Fluorescence decays of *exo*-**1** and **3** in dichloromethane, λ_{ex} = 345 nm λ_{em} = 400 nm. [*exo*-**1**] = [**3**] = 1.0 × 10^{-5} M.

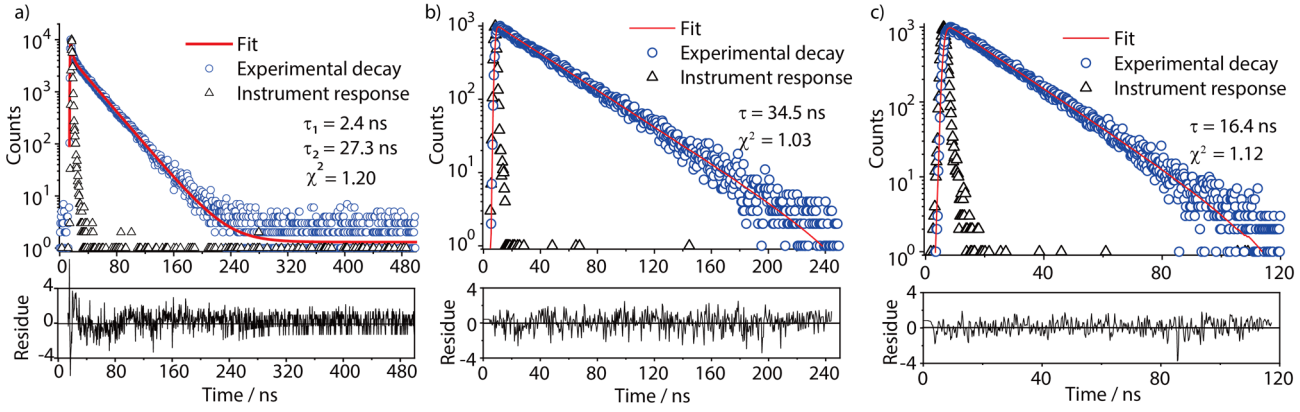

Fig. S22 Fluorescence decays of a) *exo*-**2**, λ_{ex} = 340 nm, λ_{em} = 400 nm; b) **3**, λ_{ex} = 340 nm, λ_{em} = 400 nm; c) **4,** λ_{ex} = 345 nm, λ_{em} = 510 nm in dichloromethane. [*exo*-**2**] = [**3**] = [**4**] = 1.0 × 10^{-5} M.

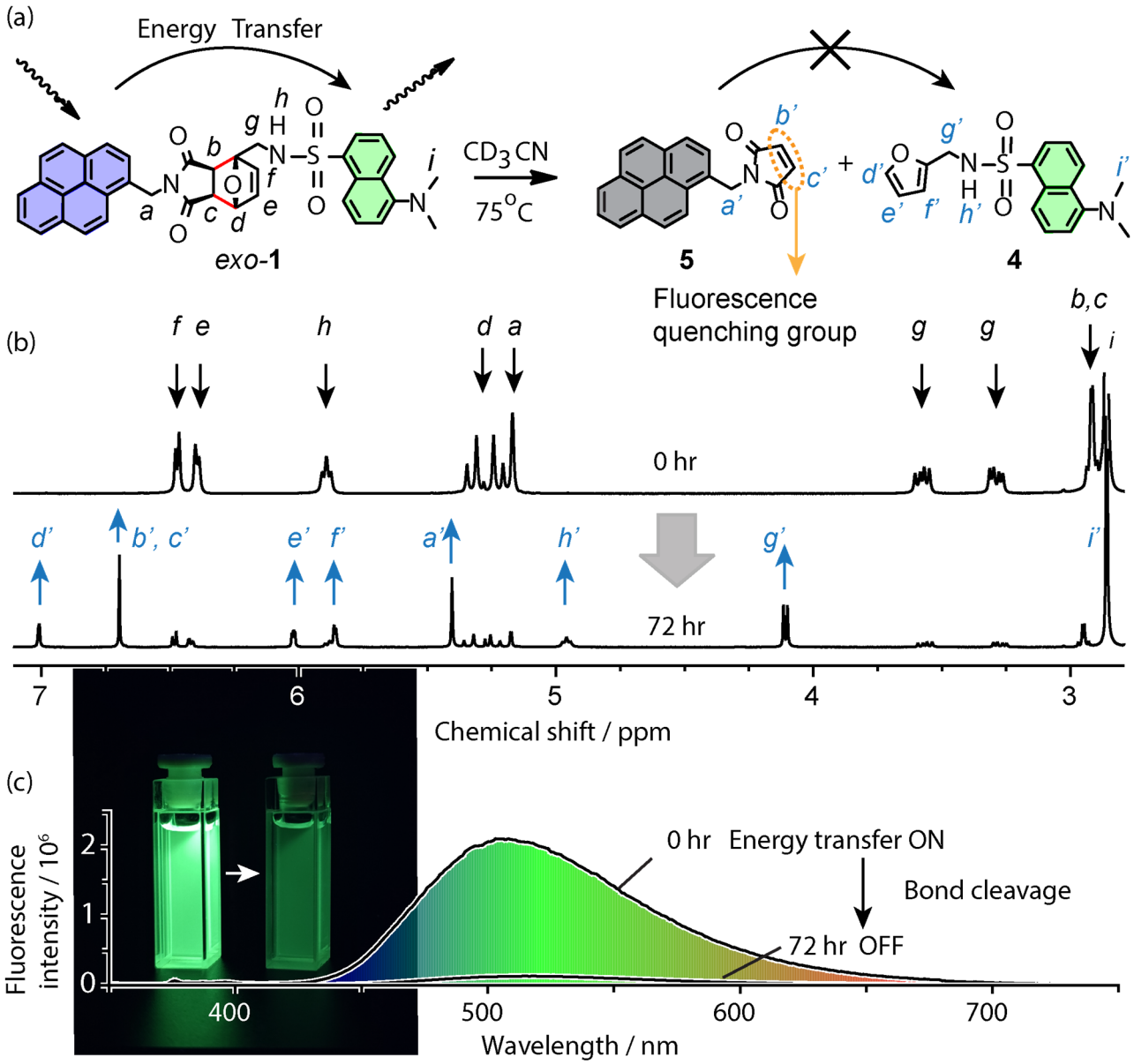

Fig. S23 a) Chemical structures of *retro* Diels-Alder addition reaction of *exo*-**1**. b) Diels-Alder covalent bond cleavage monitoring by ^{1}H NMR spectroscopy before (0 h, top) and after (72 h, bottom) *retro* Diels-Alder addition reaction in CD_3CN at 75 °C. c) The change of fluorescence spectra before (0 h) and after (72 h) Diels-Alder covalent bond cleavage. Fluorescence spectra were measured in diluted CH_2Cl_2 solution (2 x 10^{-5} M) at room temperature. λ_{ex} = 277 nm.

6. References

(1) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, 2006, pp. 205-472.

(2) B. Valeur and M. N. Berberan-Santos, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Germany, 2012, pp. 109-138.