Supplementary Information

Bioinspired synthesis of pentalene-based chromophores from an oligoketone chain

Yuki Saito, Masayuki Higuchi, Shota Yoshioka, Hisanori Senboku and Yasuhide Inokuma

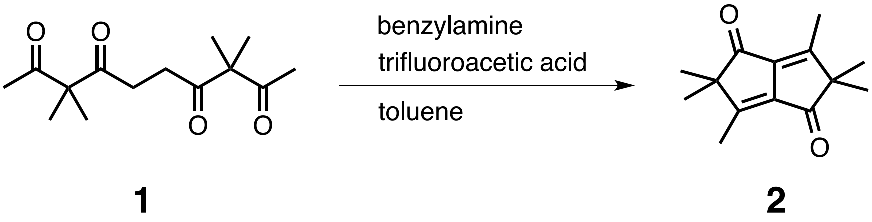
Table of contents

I. Reagents and Equipment

Solvents and reagents were purchased from WAKO Pure Chemical Industries Ltd., TCI Co., Ltd., or Sigma-Aldrich Co., and used without further purification. All the ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JMN-ECS400 spectrometer (400 MHz) at 300 K and the chemical shifts are reported in parts per million (ppm) relative to an internal standard tetramethylsilane ($\delta = 0.00$ ppm for ^{1}H and ^{13}C) in $CDCl_3$. ESI-TOF-MS spectra were recorded on a Thermo scientific Exactive spectrometer for organic compounds. Infrared spectra were measured using a JASCO Co. FT/IR-4700. Absorption spectra were recorded on a Hitachi U-2910 spectrometer. Absolute fluorescence quantum yields were determined on HAMAMATSU C9920-02S. Cyclic voltammetry was carried out by a HOKUTO DENKO HSV-100 using a GC disk electrode (Φ 1.6 mm) as a working electrode, a Pt wire (Φ 0.5 mm) as a counter electrode, and $Ag/Ag^{+}/CH_3CN/Bu_4NPF_6$ (0.01 M $AgNO_3$ in 0.1 M Bu_4NPF_6 in CH_3CN) as a reference, respectively. Elemental analysis was performed using a Exceter Analytical, Inc. CE440. Thin layer chromatography (TLC) was performed on a silica gel sheet, MERCK silica gel 60 F254. Preparative scale separations were carried out using silica gel gravity column chromatography (Wako gel C-300).

II. Experimental Details and Spectral Data

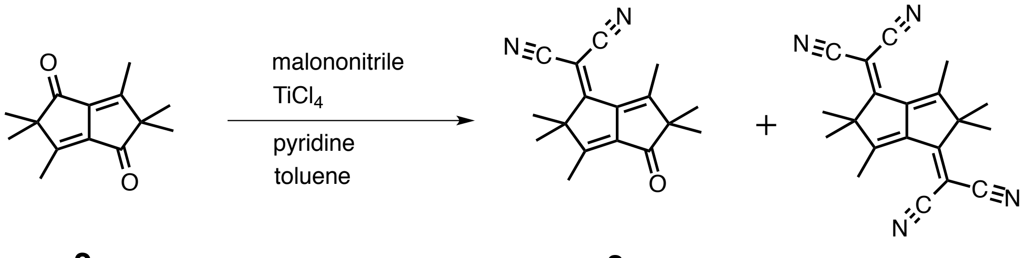
Synthesis of 2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1,4-dione (2).



To a 300 mL round bottomed flask equipped with a water separator (Dean-Stark apparatus) and a reflux condenser were added 3,3,8,8-tetramethyldecane-2,4,7,9-tetraone (**1**) (3.00 g, 11.8 mmol), benzylamine (1.29 mL, 11.8 mmol), trifluoroacetic acid (1.08 mL, 14.2 mmol) and toluene (60 mL). The reaction mixture was heated to reflux for 9 h. After the reaction mixture was cooled to room temperature, toluene (120 mL) and saturated aqueous sodium bicarbonate (120 mL) were added to the reaction mixture. The organic layer was washed with water (60 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (diameter 4.0 cm, height 16 cm, hexane : ethyl acetate = 10:1), yielding 2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1,4-dione (1.38 g, 6.32 mmol) as a yellow solid in 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.08 (s, 6H, 3- and 6-methyl), 1.19 (s, 12H, 2- and 5-dimethyl); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 205.7, 149.6, 137.5, 60.4, 21.9, 11.7; IR (ATR, neat): 3417, 2962, 2926, 2866, 2356, 2340, 1708, 1638, 1455, 1428, 1367, 1141, 1096, 980 cm^{-1}; mp 122-125 °C; HR-ESI-TOF MS: *m/z* = 219.1380 (Calculated for $C_{14}H_{19}O_2$, 219.1380 $[M+H]^+$); Elemental analysis (%): C, 76.99; H, 8.36; N, 0.00. (Calculated for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; N, 0.00). R_f = 0.28 (eluent: hexane/ethyl acetate = 10:1). UV/Vis (acetonitrile): λ_{max} (ε) 281 nm (23400 L mol^{-1} cm^{-1}), 293 (23500).

Knoevenagel reaction of pentalene analogue 2



2 **3** **4**

(i) Protocol with $TiCl_4$/pyridine

2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1,4-dione (**2**) (1.00 g, 4.58 mmol) and malononitrile (1.82 g, 27.5 mmol) were dissolved in toluene (200 mL) in 300 mL round bottom flask. Then pyridine (1.29 mL, 16.0 mmol) and titanium tetrachloride (1.76 mL, 16.0 mmol) were added to the solution of **2**. The reaction mixture was stirred at 80 °C under nitrogen atmosphere. After 19 h stirring, malononitrile (606 mg, 9.17 mmol), pyridine (0.50mL, 4.58mmol) and titanium tetrachloride (0.37 mL, 4.58 mmol) were added to the flask and stirred for 7 h. After cooling to room temperature the reaction solution was filtered. The filtrate was washed with water (150 mL), dried over anhydrous sodium sulfate, and the solvent was removed by a rotary evaporator. The residue was separated by silica gel column chromatography (diameter 3.0 cm, height 21.0 cm, hexane : ethyl acetate = 6 : 1) to give compound **3** (183 mg, 0.69 mmol) as a yellow crystals in 15% yield and compound **4** (592 mg, 1.88 mmol) as a yellow crystals in 41% yield. A sample for UV-Vis measurement was obtained by recrystallization from hexane.

(ii) Protocol with AcOH/$AcONH_4$

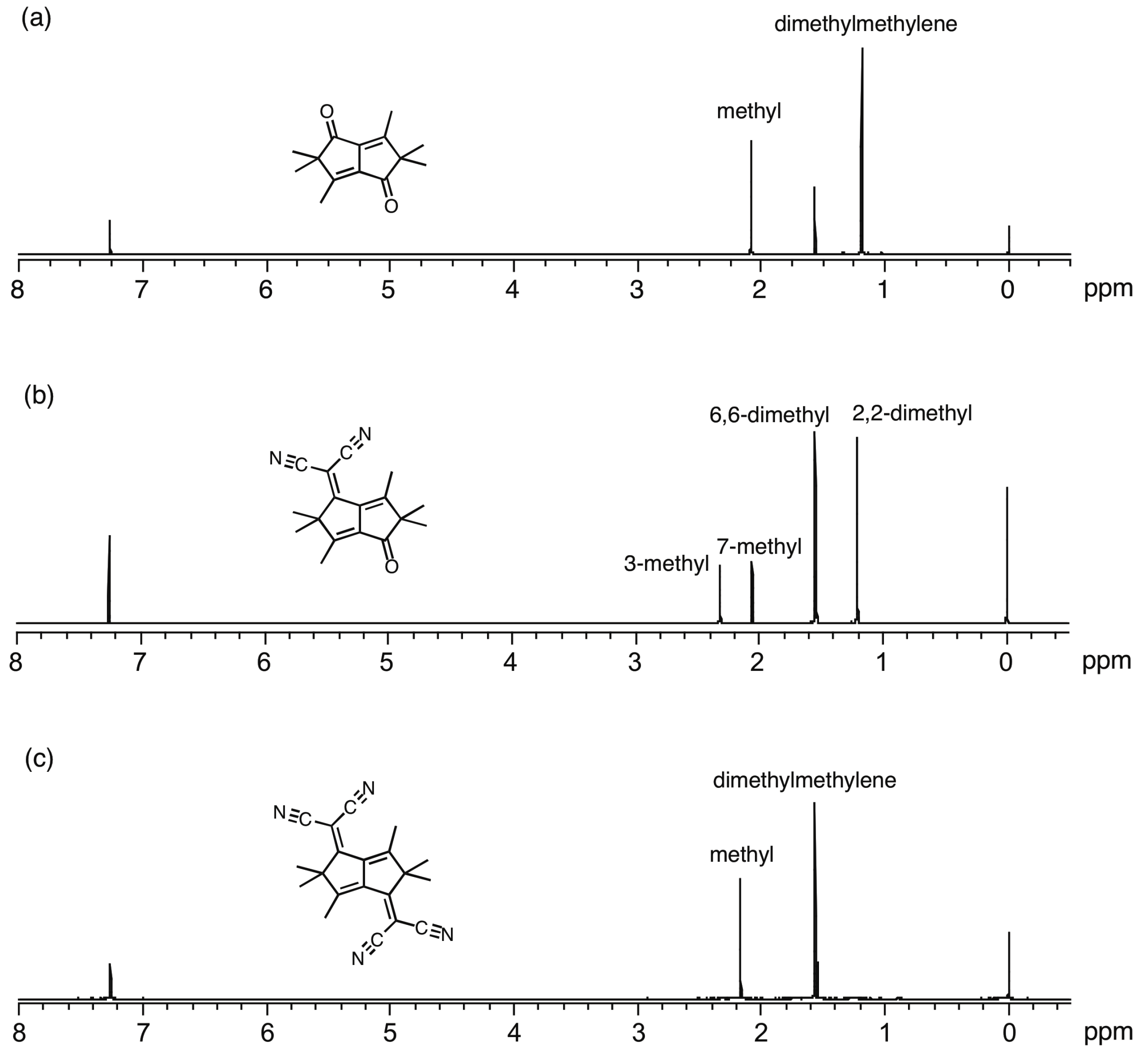
2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1,4-dione (**2**) (500 mg, 2.29 mmol) and malononitrile (303 mg, 4.59 mmol) and toluene (1.43 mL) were added to the 10 mL flask. Then ammonium acetate (106 mg, 1.37 mmol) and acetic acid (432 μL, 7.55 mmol) were added, the flask was equipped with a reflux condenser and a Dean–Stark trap. The reaction mixture was heated at 130 °C for 4 h. After cooling to room temperature, toluene (5 mL) and saturated aqueous sodium bicarbonate (2.5 mL) were added to the flask. The solution in the flask were moved to a separation funnel, the organic layer was separated and washed with water (2.5 mL), dried over anhydrous sodium sulfate, and the solvent was removed by a rotary evaporator. The residue was separated by silica gel column chromatography (diameter 4.0 cm, height 13.0 cm, hexane : ethyl acetate = 6 : 1) to give compound **3** (168 mg, 0.63 mmol) as a yellow crystals in 28% yield and compound **4** (94 mg, 0.30 mmol) as a yellow crystals in 13% yield.

2-(2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1-one-4-ylidene)malononitrile (3).

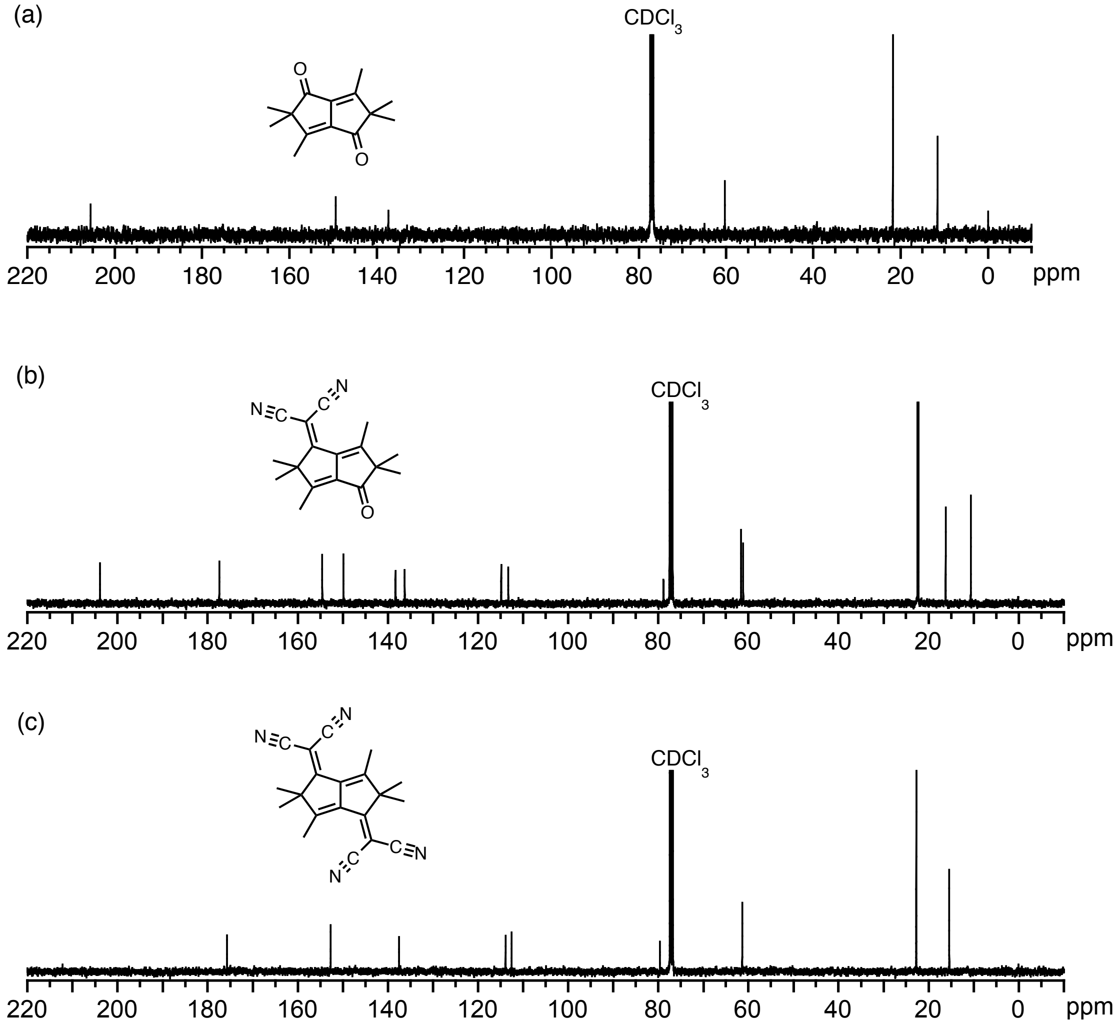
^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 2.32 (s, 3H, 3-methyl), 2.06 (s, 3H 6-methyl), 1.55 (s, 6H, 5-dimethyl), 1.21 (s, 6H, 2-dimethyl); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 203.9, 177.5, 154.6, 149.9, 138.3, 136.3, 114.9, 113.3, 78.9, 61.7, 61.1, 22.5, 22.3, 16.2, 10.6; IR (ATR, neat) 2971, 2927, 2867, 2364, 2226, 1712, 1661, 1591, 1561, 1463, 1430, 1149 cm^{-1}; mp 172-190 °C (decomp.); HR-ESI-TOF MS: *m/z* = 265.1351 (calculated for $C_{17}H_{18}N_2O$, 265.1346 $[M-H]^-$); Elemental analysis (%): C, 76.68; H, 6.82; N, 10.48. (Calculated for $C_{14}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52) ; R_f = 0.25 (eluent: hexane/ethyl acetate = 6:1) ; UV/Vis (acetonitrile): λ_{max} (ε), 393 nm (5360 L mol^{-1} cm^{-1}), 300 (12400).

2,2'-(2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1,4-diylidene)dimalononitrile (4).

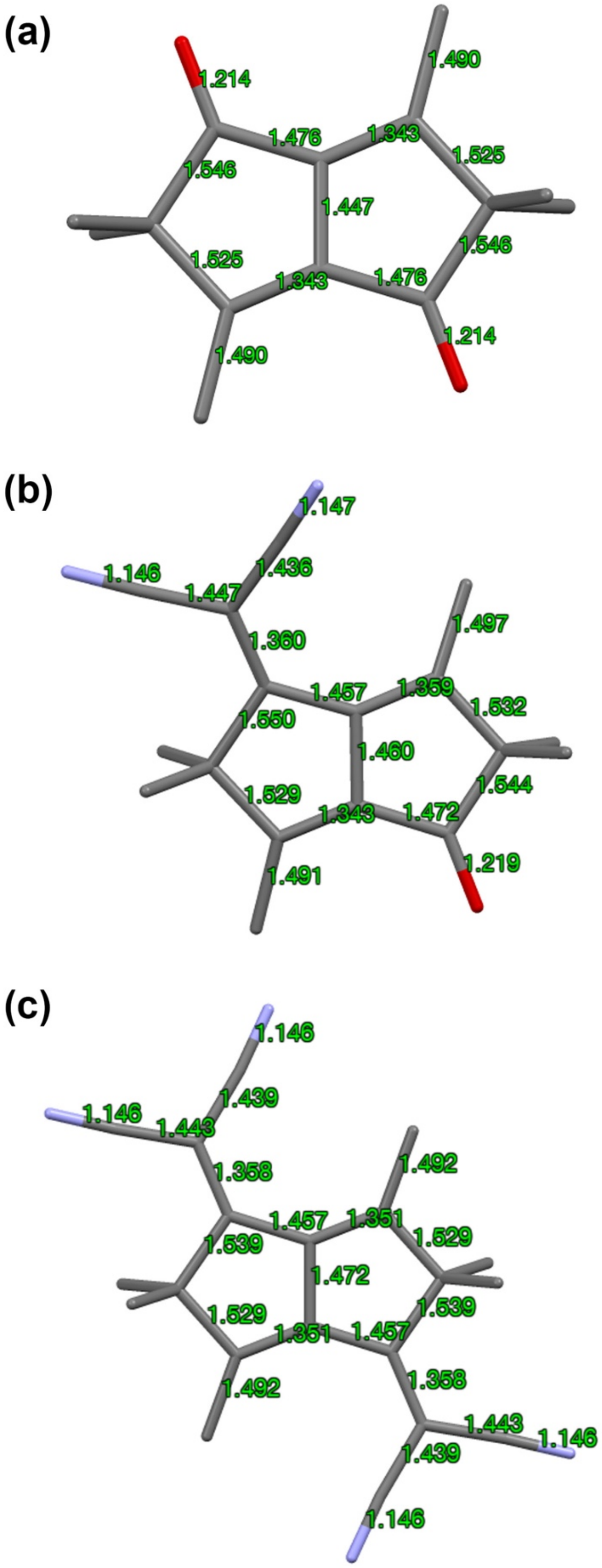
^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (s, 6H, 3- and 6-methyl), 1.56 (s, 12H, 2- and 5-dimethyl); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 175.8, 152.8, 137.6, 114.0, 112.6, 79.7, 61.4, 22.8, 15.5; IR (ATR, neat) 2984, 2875, 2364, 2341, 2220, 1739, 1616, 1573, 1464, 1442, 1430, 1364, 1153, 1113 cm^{-1}; mp 220-223 °C (decomp.); HR-ESI-TOF MS: *m/z* = 313.1461 (calculated for $C_{20}H_{18}N_4$, 313.1459 $[M-H]^-$); Elemental analysis (%): C, 76.31; H, 5.70; N, 17.76 (Calculated for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77, N, 17.82) ; R_f = 0.11 (eluent: hexane/ethyl acetate = 6:1) ; UV/Vis (acetonitrile): λ_{max} (ε), 355 nm (14800 L mol^{-1} cm^{-1}), 279 (17000), 207 (16000).



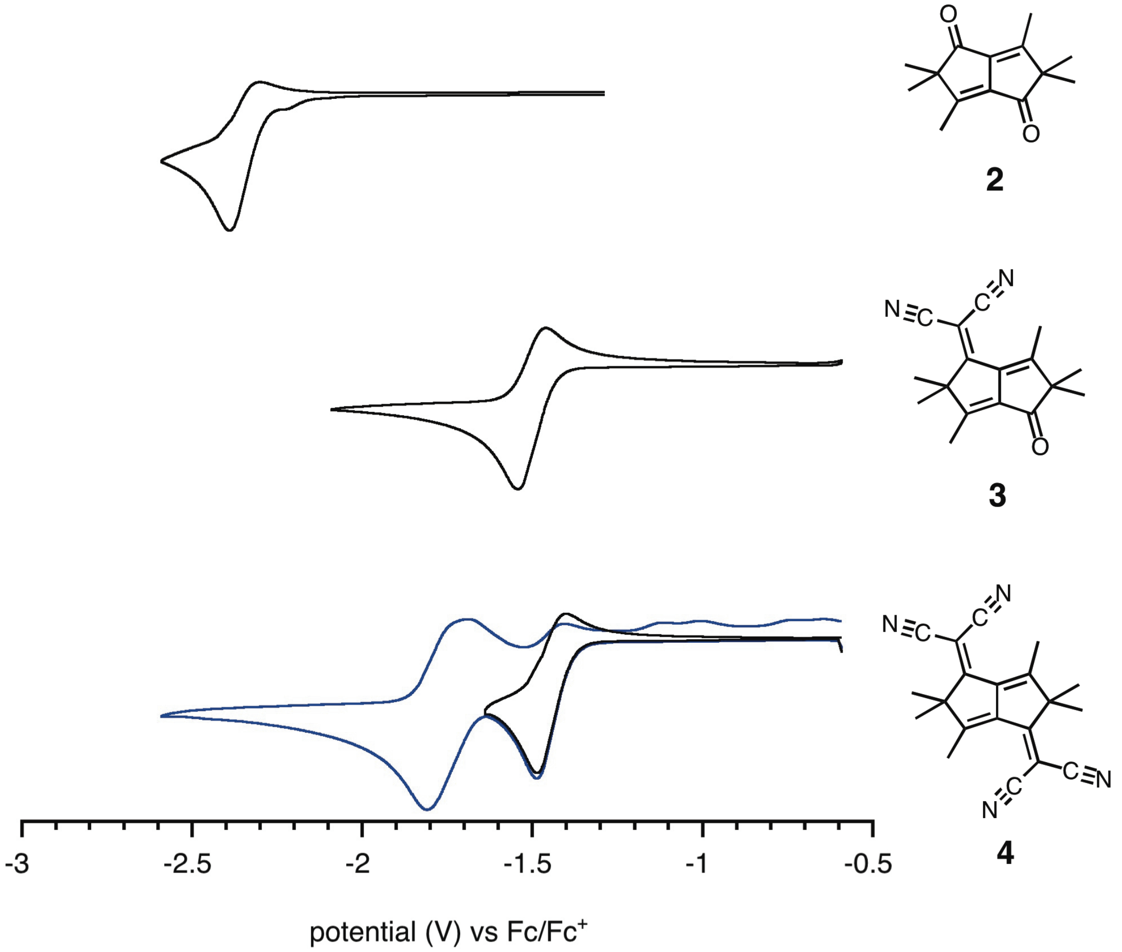
Supplementary Figure 1. ^{1}H NMR spectra of pentalene analogues (a) compound **2**, (b) compound **3** and (c) compound **4** in $CDCl_3$.



Supplementary Figure 2. ^{13}C NMR spectra of pentalene analogues (a) compound **2**, (b) compound **3** and (c) compound **4** (in $CDCl_3$).



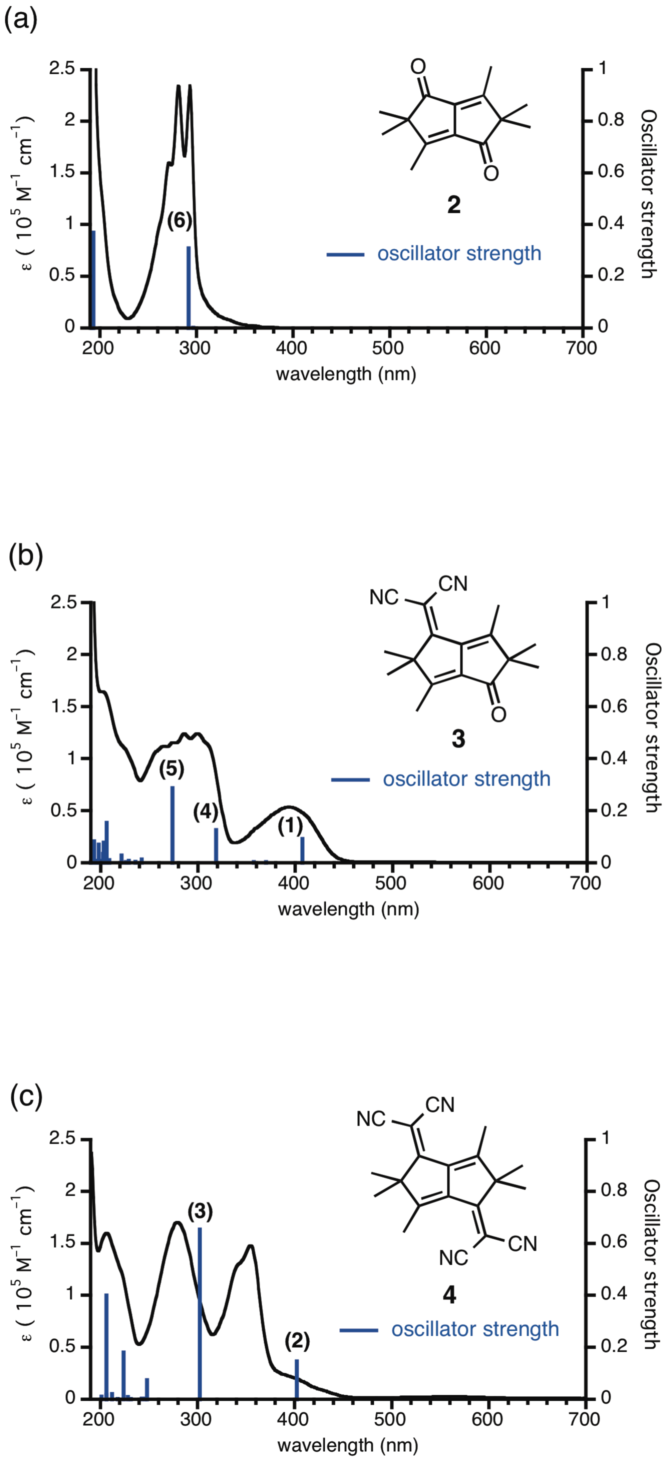
Supplementary Figure 3. Selected bond lengths in Å for pentalene analogues **2–4** obtained by X-ray diffraction analysis.



compound	$E^{1}_{1/2}$ (V)	$E^{2}_{1/2}$ (V)
2	-2.35	—
3	-1.50	—
4	-1.46	-1.75

Supplementary Figure 4. Cyclic voltammograms of pentalene analogues **2**, **3** and **4** measured in acetonitrile at 3.0 mM using tetrabutylammonium hexafluorophosphate (10 mM) as supporting electrolyte (E/V vs. ferrocene/ferrocenium cation, scan rate 100 mVs^{-1}).

While compound **4** showed a quasi-reversible reduction wave when scanned in the range of –0.6 ~ –1.6 V, it became irreversible and some other minor peaks along with the second reduction wave were observed when scanned in the range of –0.6 ~ –2.6 V.



transition (1) (359.70 nm, f = 0.0000)
HOMO-1 --> LUMO (77%)
HOMO-2 --> LUMO+1 (22%)

transition (2) (356.74 nm, f = 0.0000)
HOMO-1 --> LUMO+1 (70%)
HOMO-2 --> LUMO (29%)

transition (3) (321.54 nm, f = 0.0000)
HOMO --> LUMO+1 (98%)

transition (4) (297.62 nm, f = 0.0000)
HOMO-2 --> LUMO (71%)
HOMO-1 --> LUMO+1 (29%)

transition (5) (296.40 nm, f = 0.0011)
HOMO-2 --> LUMO+1 (76%)
HOMO-1 --> LUMO (23%)

transition (6) (291.93 nm, f = 0.3081)
HOMO --> LUMO (96%)
HOMO-3 --> LUMO+1 (4%)

transition (1) (407.40 nm, f = 0.0909)
HOMO --> LUMO (90%)
HOMO --> LUMO+1 (6%)
HOMO-2 --> LUMO (3%)

transition (2) (370.11 nm, f = 0.0017)
HOMO-1 --> LUMO (90%)
HOMO-1 --> LUMO+1 (8%)

transition (3) (357.35 nm, f = 0.0021)
HOMO-1 --> LUMO+1 (85%)
HOMO-1 --> LUMO (9%)
HOMO --> LUMO+1 (4%)

transition (4) (318.75 nm, f = 0.1250)
HOMO --> LUMO+1 (85%)
HOMO --> LUMO (5%)
HOMO-1 --> LUMO+1 (4%)
HOMO-2 --> LUMO+1 (3%)

transition (5) (273.90 nm, f = 0.2863)
HOMO-2 --> LUMO (92%)
HOMO --> LUMO (4%)

transition (1) (449.25 nm, f = 0.0000)
HOMO --> LUMO (97%)
HOMO-1 --> LUMO+1 (3%)

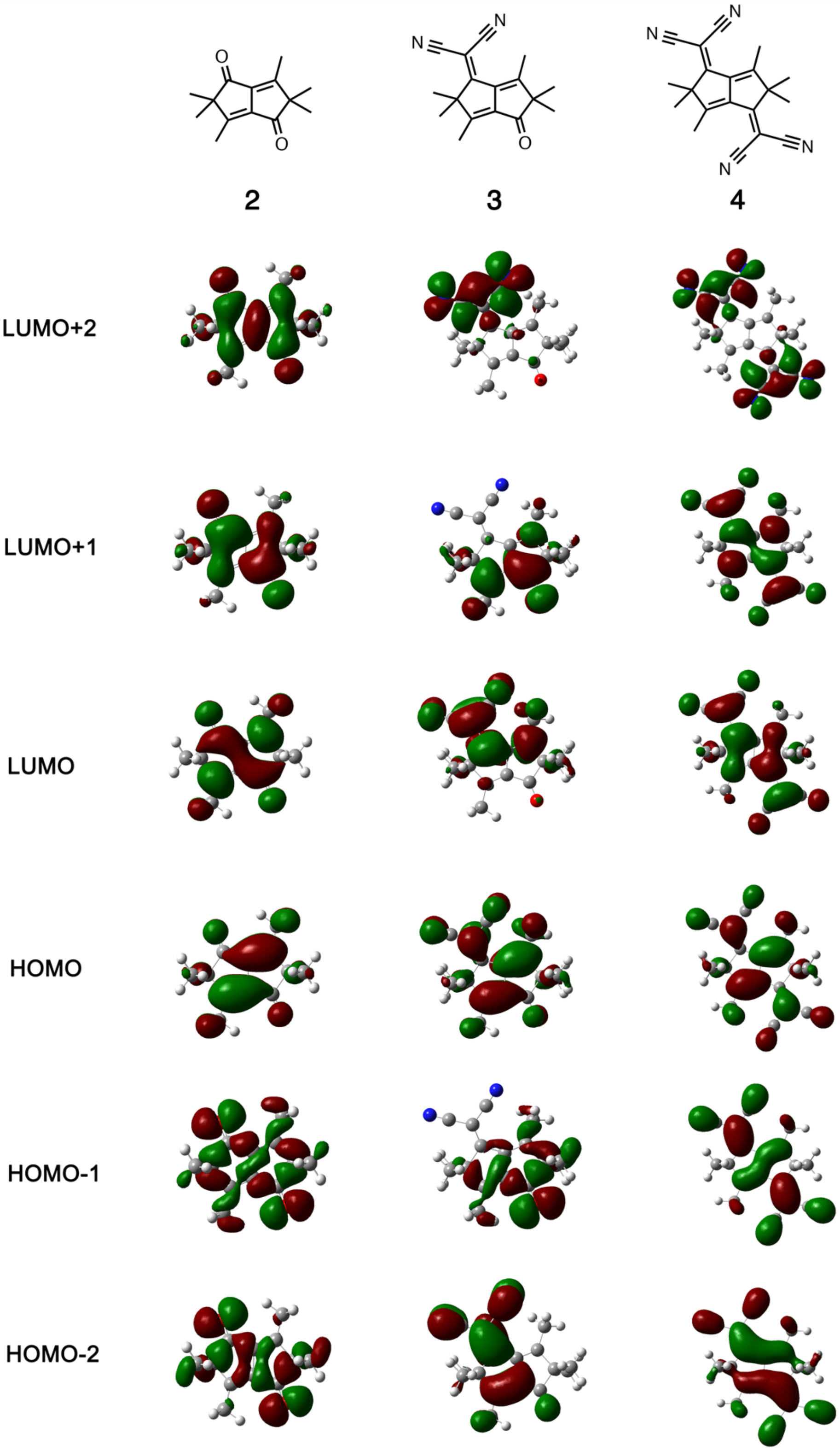
transition (2) (402.13 nm, f = 0.1459)
HOMO --> LUMO+1 (93%)
HOMO-1 --> LUMO (7%)

transition (3) (302.56 nm, f = 0.6532)
HOMO-1 --> LUMO (92%)
HOMO --> LUMO+1 (7%)

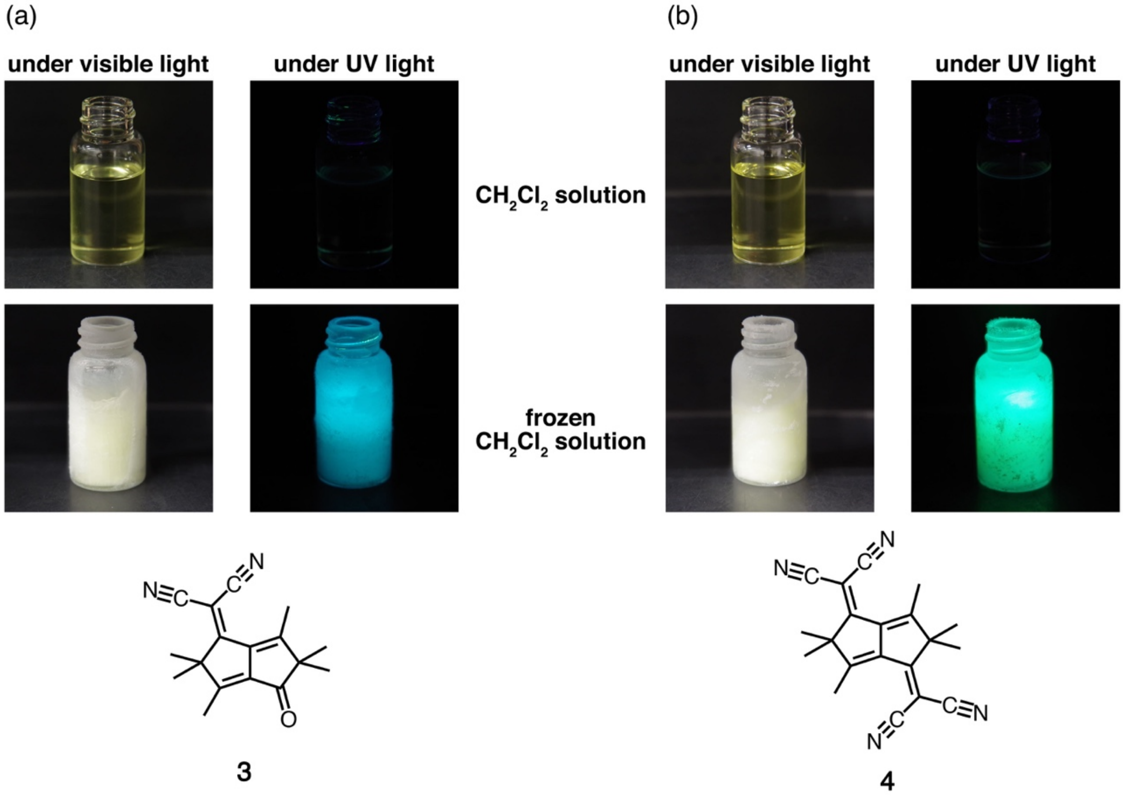
transition (4) (298.53 nm, f = 0.0000)
HOMO --> LUMO+2 (94%)
HOMO-1 --> LUMO+1 (3%)
HOMO-1 --> LUMO (3%)

transition (5) (248.07 nm, f = 0.0738)
HOMO-1 --> LUMO+1 (79%)
HOMO --> LUMO+4 (18%)

Supplementary Figure 5. Observed (black line) and calculated (blue bar) absorption spectra of pentalene analogues (a) **2**, (b) **3**, and (c) **4**. TD-DFT calculations were performed at the B3LYP/6-31G(d) level. Characters of several low-energy transitions were listed in the right column.



Supplementary Figure 6. orbital density diagrams of frontier orbitals for pentalene analogues **2**–**4** calculated at the B3LYP/6-31G(d) level.



Supplementary Figure 7. Photographs of (top) dichloromethane solution and (bottom) frozen dichloromethane solution of compound (a) **3** and (b) **4** under visible light (left column) and UV light (365 nm) irradiation (right column).