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Supporting Information

Cardo Bisphenol Fluorene Fused with Dibenzo[*g*,*p*]chrysene for a High Refractive Index Monomer

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1. Materials and Methods

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. All reactions were carried out under an argon or a nitrogen atmosphere in dried glassware using standard vacuum-line technique, unless otherwise noted. All work-up operation and purification procedures were carried out with reagent-grade solvent in air, and analytical thin layer chromatography was carried out on Merck silica 60F₂₅₄ pre-coated plates. The developed chromatogram was analyzed by UV lamp (254 nm or 354 nm). Flash column chromatography was carried out with silica gel 60 N (Kanto Chemical Co.). All melting points were recorded on the melting point apparatus of "Stanford Research Systems OptiMelt" and are not corrected. IR spectra were reported with a JASCO FT/ IR-6000 infrared spectrometer and the data are expressed in cm⁻¹. High-resolution mass spectra (HRMS) were determined on the basis of TOF (time of flight)-MS (MALDI-TOF or LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZ400S (1H 400 MHz and ¹³C 100 MHz) spectrometer. Chemical shifts for ¹H NMR are expressed in parts per million (ppm) relative to CHCl₃ (7.26), CD₃CN (1.94), DMSO (2.50). Chemical shifts for ¹³C NMR are expressed in ppm relative to CDCl₃ (77.0), CD₃CN (1.32), [D6]-DMSO (39.5). Data are reported as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constants (Hz), and integration. X-ray single crystal diffraction analyses were performed on a Rigaku XtaLab P200 diffractometer Cu-Ka radiation. Data collection, cell refinement, data reduction and analysis were carried out with the CrysAlisPro (Rigaku Oxford Diffraction), in which the structures were solved by intrinsic phasing methods with the

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SHELXT program and refines using SHELXL¹ with anisotropic displacement parameters for non-H atoms. CCDC numbers contain the supplementary crystallographic data for this paper, and the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data request/cif. Thermogravimetric analysis (TGA) was performed with a TA instrument SDT Q600 under argon flow at a heating rate of 10 °C min⁻¹. UV-vis absorption and fluorescence spectra in the solution state were recorded on a JASCO V-770 spectrophotometer and a JASCO FP-8300 spectrophotometer, respectively. Absolute fluorescence quantum yields (QY) were determined on a Hamamatsu Photonics absolute PL quantum yield spectrometer C11347. RI were performed with KYOTO ELECTRONICS RA-620 using LED Na-D line (589.3 nm) as light source at 20 °C, and its calibration with distilled water was carried out before measurement. Quantum chemical calculations were carried out using the Gaussian 09, Revision E.01 suite of programs with default thresholds and algorism.² The geometry optimizations of all compounds in the ground state were performed at the B3LYP/6-31G(d,p) level of theory. The stationary point in the lowest singlet state was optimized without any assumption and characterized by frequency analysis at the same level of theory (the

¹ Sheldrick, G. M. A. Short History of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122.

² Gaussian 09 (Revision E.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

number of imaginary frequencies was 0). The cartesian coordinates are given in Table S1.

2. Experimental Procedures

1) Synthesis of 2 (Scheme 2). For 2,7-Di-tert-butyl-9H-fluorene-4-carbaldehyde. Under



an argon atmosphere, to a solution of 2,7-di-*tert*-butylfluorene (10 g, 36 mmol) in dry CH₂Cl₂ (40 mL) at 0 °C was added dichloromethyl methyl ether (4.0 mL, 43 mmol), then tin(IV) chloride (8.0 mL, 72 mmol) was slowly added over 3 min. After

stirred at room temperature for 0.5 h, the reaction was quenched with water (40 mL) and satd. aq. NaHCO₃ (40 mL) at 0 °C. The aqueous layer was extracted with CH₂Cl₂ (50 mL x 3). The combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give 11 g of crude products as white (colorless) solid materials. Purification by short-plugged silica-gel column chromatography (hexane/toluene, 1:1) afforded 11 g of the target aldehyde as white (colorless) solid materials (97%). Data: R_f value 0.36 (hexane/EtOAc, 19:1); ¹H NMR (400 MHz, CDCl₃) 10.68 (s, 1H, CHO), 8.40 (d, J = 8.4 Hz, 1H, H-5), 7.90 (d, J = 1.9 Hz, 1H, H-8), 7.78 (d, J = 1.6 Hz, 1H, H-3), 7.61 (d, J = 1.6 Hz, 1H, H-1), 7.46 (dd, J = 8.4, 1.9 Hz, 1H, H-6), 3.93 (s, 2H, CH₂), 1.41 (s, 9H, CH₃), 1.39 (s, 9H, CH₃) ppm.

For 2,7-Di-tert-butyl- 9-oxo-9H-fluorene-4-carboxylic acid. To a solution of the



starting aldehyde (1.0 g, 3.3 mmol) in pyridine (10 mL) was added FeCl₃·6H₂O (180 mg, 0.65 mmol), then *tert*-butyl hydroperoxide (TBHP, 70% in H₂O, 4.0 mL, 29 mmol) was slowly added over 5 min. After stirred at 80 °C for 16 h, the reaction mixture was

allowed to cool to ambient temperature. The mixture was filtered through a pad of celite and silica-gel (EtOAc), and the filtrate was thoroughly evaporated off. The resultant residue was diluted with EtOAc (20 mL), which was transferred into a 200 mL

separatory funnel and washed with H₂O (100 mL) and brine (100 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give 1.2 g of crude products. Purification by short-plugged silica-gel column chromatography (EtOAc only) gave 1.0 g (92%) of the target carboxylic acid as orange solid materials. Data: R_f value 0.14 (hexane/ EtOAc, 2:1); M.p. 229-230 °C; ¹H NMR (400 MHz, CDCl₃) 8.33 (d, J = 8.2 Hz, 1H, H-5), 8.15 (d, J = 2.1 Hz, 1H, H-3), 7.94 (d, J = 2.1 Hz, 1H, H-1), 7.78 (d, J = 2.0 Hz, 1H, H-8), 7.57 (dd, J = 8.2 Hz, 2.0 Hz, 1H, H-6), 1.40 (s, 9H, CH₃), 1.36 (s, 9H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) 193.8 (C=O), 172.5 (CO₂H), 153.4 (C-7), 152.2 (C-2), 142.6 (C-4b), 140.4 (C-8a), 136.4 (C-4a), 134.9 (C-9a), 133.6 (C-1), 132.1 (C-3), 126.2 (C-6), 125.9 (C-4), 124.7 (C-5), 121.4 (C-8), 35.0 (\underline{C} (CH₃)₃, two peaks are overlapped), 31.0 (CH₃), 31.0 (CH₃) ppm; MS (DART-TOFMS) *m/z*: 337 [MH]+; IR (neat): 2953, 2550 (COOH), 1717, 1685, 1459, 1243, 1178, 783 cm⁻¹; HRMS (DART-TOF) calcd. for C₂₂H₂₅O₃: 337.1804 [MH]+, found: 337.1793.

For 2, Methyl 2,7-di-tert-butyl-9-oxo-9H-fluorene-4-carboxylate. To a solution of the



starting carboxylic acid (4.0 g, 12 mmol) in *N*,*N*-dimethylformamide (40 mL) was added lithium carbonate (4.4 g, 59 mmol) and iodomethane (3.7 mL, 59 mmol). After stirred at room temperature for 15 h, the reaction was guenched with satd. aq. NH₄Cl (60 mL)

at 0 °C. The mixture was transferred into a 200 mL separatory funnel, and aqueous phase was extracted with toluene (50 mL x 3), and the combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give 4.0 g of crude products. Recrystallization from EtOH (12 mL, 3.0 mL/g) gave 3.2 g of **2** in 74% yield as yellow solid materials. Data: R_f value 0.57 (hexane/EtOAc, 9:1); M.p. 137-138 °C; ¹H NMR (400 MHz, CDCl₃) 8.33 (d, J = 8.1 Hz, 1H, H-5), 7.93 (d, J = 2.0 Hz, 1H, H-3), 7.86 (d, J = 2.0 Hz, 1H, H-1), 7.74 (d, J = 2.0 Hz, 1H, H-8), 7.52 (dd, J = 8.1 Hz, 2.0Hz, 1H, H-6), 4.01 (s, 3H, OCH₃), 1.36 (s, 9H, CH₃), 1.35 (s, 9H, CH₃)

ppm; ¹³C NMR (100 MHz, CDCl₃) 193.8 (C=O), 167.5 (<u>C</u>O₂CH₃), 153.1 (C-7), 152.0 (C-2), 141.5 (C-4b), 140.6 (C-8a), 136.1 (C-9a), 134.9 (C-4a), 132.6 (C-1), 131.9 (C-3), 125.9 (C-4), 125.5 (C-6), 124.7 (C-8), 121.3 (C-5), 52.4 (CO₂<u>C</u>H₃), 34.9 (<u>C</u>(CH₃)₃, two peaks are overlapped), 31.04 (CH₃), 30.96 (CH₃) ppm; MS (DART-TOFMS) *m/z*: 351 [MH]+; IR (neat): 2952, 1706 (C=O), 1457, 1238, 1185, 1154, 1079, 786, 558 cm⁻¹; HRMS (DART-TOF) calcd. for C₂₃H₂₇O₃: 351.1960 [MH]+, found: 351.1951; Anal. Calcd for C₂₃H₂₆O₃; C, 78.83; H, 7.48. Found: C, 78.68; H,7.57.

2) Synthesis of 3 via 5 (Scheme 3). For 5, Methyl (±)-2',7'-dibromo-2,7-di-*tert*-butyl-10' oxo-10'*H*-spiro[fluorene-9,9'-phenanthren]-4-carboxylate. Under an argon



atmosphere, the starting ester **2** (12 g, 34 mmol) and 2,7dibromo-9*H*-fluoren-9-one (23 g, 69 mmol) were suspended in $P(O_IPr)_3$ (94 mL, 410 mmol), and the mixture was heated to 110 °C (bath set to 130 °C). After stirred for 14 h, the reaction mixture was cooled to 60 °C, and water (95 mL) was added over

5 min, and re-heated to 80 °C for hydrolyzing the residual P(O/Pr)₃. After stirred for additional 2 h, the reaction mixture was cooled to room temperature. The mixture was diluted with toluene (200 mL), and the aqueous layer was extracted with toluene (30 mL × 3). The combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give orange oil. Treatment with short-plugged silica-gel column chromatography (hexane/toluene, 1:1) gave 26 g (quant.) of **5** as orange solid materials. Data of **5**: *Rt* value 0.35 (hexane/CHCl₃, 1:1); M.p. 221-224 °C; ¹H NMR (400 MHz, CDCl₃) 8.27 (d, *J* = 8.4 Hz, 1H, H-5), 8.07 (d, *J* = 2.0 Hz, 1H, H-1'), 8.02 (d, *J* = 8.6 Hz, 1H, H-4'), 7.91 (d, *J* = 8.4 Hz, 1H, H-5'), 7.90 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H, H-3'), 7.51 (dd, *J* = 8.4, 1.9 Hz, 1H, H-6'), 7.41 (dd, *J* = 8.4, 1.9 Hz 1H, H-6), 7.16 (d, *J* = 2.0 Hz, 1H, H-1), 6.93 (d, *J* = 1.9 Hz, 1H, H-8'), 4.04 (s, 3H, OCH₃), 1.23 (s, 9H, CH₃), 1.16 (s,

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9H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) 194.7 (C=O), 168.1 (*Q*O₂CH₃), 151.5 (C-7), 150.2 (C-2), 147.1 (C-8a'), 146.0 (C-8a), 141.2 (C-3'), 138.2 (C-9a), 137.4 (C-5), 136.8 (C-10a'), 135.8 (C-4b), 131.2 (C-1'), 131.0 (C-8'), 130.8 (C-4a, C-4a', two peaks are overlapped), 128.7 (C-4), 127.4 (C-1), 125.8 (C-5'), 125.7 (C-4b'), 125.3 (C-6'), 125.0 (C-7'), 124.8 (C-2'), 124.6 (C-8), 123.4 (C-3), 122.5 (C-6), 120.4 (C-4'), 67.6 (C-9), 51.9 (OCH₃), 34.47 (*Q*(CH₃)₃), 34.43 (*Q*(CH₃)₃), 30.82 (CH₃), 30.80 (CH₃) ppm; MS (DART-TOFMS) *m/z*: 670 [M]+; IR (neat): 2952, 1717 (C=O), 1677 (C=O), 1589, 1461, 1292, 1245, 1225, 1153, 810, 798, 742 cm⁻¹; HRMS (DART-TOFMS) calcd. for C₃₆H₃₂⁷⁹Br₂O₃: 670.0718 [M]+, found; 670.0713; Anal. Calcd for C₃₆H₃₂Br₂O₃; C, 64.30; H, 4.80. Found: C, 64.44; H, 4.86.

For **3**, **Methyl 6,11-dibromo-3,14-di-***tert*-**buty-dibenzo**[*g*,*p*]**chrysene**. Under an argon



atmosphere, to a solution of the starting **5** (21 g, 31 mmol) in toluene (100 mL) was added methanol (20 mL). The flask was heated at 45 °C, and then NaBH₄ (480 mg, 13 mmol) was added at 5 min intervals (7 times in all). After the mixture was stirred for 0.5 h, the reaction was quenched with acetone (4.0 mL) and conducted for additional 15 min stirring. The organic layer was

washed with water (100 mL x 3), and transferred into a 100 mL flask, and the flask was heated at 130 °C for azeotropic removal of water, which was followed by addition of methanesulfonic acid (0.02 mL, 0.32 mmol). After stirred for 0.5 h, the reaction mixture was allowed to cool to room temperature. The mixture was washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give crude products of orange solid materials. Purification by short-plugged silica-gel column chromatography (hexane/CHCl₃, 1:1) gave 20 g (93% in 2 steps) of **3** as orange solid materials. Data: R_f value 0.71 (hexane/CHCl₃, 2:1); M.p. 331-334 °C; ¹H NMR (400 MHz, CDCl₃) 8.91 (d, *J* = 1.9 Hz, 1H, H-4), 8.75 (d, *J* = 1.9 Hz, 1H, H-5), 8.73 (d, *J* = 1.9 Hz, 1H, H-12), 8.56

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(d, J = 1.8 Hz, 1H, H-13), 8.51 (d, J = 8.8 Hz, 2H, H-8, H-9, two peaks are overlapped), 8.04 (d, J = 8.6 Hz, 1H, H-16), 7.87 (d, J = 1.9 Hz, 1H, H-2), 7.79 (dd, J = 8.8, 1.9 Hz, 1H, H-7), 7.77 (dd, J = 8.8, 1.9 Hz, 1H, H-10), 7.63 (dd, J = 8.6, 1.8 Hz, 1H, H-15), 4.01 (s, 3H, OCH₃), 1.48 (s, 9H, CH₃), 1.45 (s, 9H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) 172.3 (C=O), 150.0 (C-14), 148.8 (C-3), 131.1 (C-7), 130.9 (C-8), 130.5 (C-4c), 130.0 (C-8a) 129.9 (C-12c), 129.6 (C-9), 129.2 (C-8b, C-12a, two peaks are overlapped), 128.9 (C-16a), 128.8 (C-4b), 128.7 (C-10), 128.3 (C-12b), 127.1 (C-16), 126.8 (C-1), 126.42 (C-4a), 126.40 (C-16b), 126.3 (C-5), 125.8 (C-12), 124.9 (C-2), 124.7 (C-15), 124.3 (C-4), 123.8 (C-13), 120.8 (C-6), 120.6 (C-11), 52.4 (OCH₃), 34.8 (Q(CH₃)₃), 34.7 (Q(CH₃)₃), 31.0 (CH₃), 30.9 (CH₃) ppm; MS (DART-TOFMS) *m/z*: 654 [M]+; IR (neat): 2961, 1727 (C=O), 1469, 1285, 1248, 1138, 879, 798 cm⁻¹; HRMS (DART-TOF) calcd. for C₃₆H₃₂⁷⁹Br₂O₂: 654.0769 [M]+, found: 654.0796. Anal. Calcd for C₃₆H₃₂⁷⁹Br₂O₂; C, 65.87; H, 4.91. Found: C, 65.52; H, 4.84.

3) Synthesis of 4, 5, 6, 7, 8, and 9 (Scheme 4). For 6, 6,11-Dibromo-3,14-di-*tert* butyldibenzo[*g*,*p*]chrysene-1-carboxylic acid. To a suspension of KO*t*Bu (14 g, 130)



mmol) in dry THF (200 mL) at 0 °C was added H₂O (1.2 mL, 66 mmol). After the mixture was stirred at 0 °C for 10 min, the starting **3** (20 g, 30 mmol) was added. The reaction was conducted at 70 °C for 1 h, and quenched with 3 M aq. HCl (200 mL) at 0 °C. The mixture was diluted with EtOAc (150 mL), and the aqueous phase

was extracted with EtOAc (40 mL x 3), and the combined organic phases were washed with brine (100 mL), dried over Na₂SO₄, and concentrated *in vacuo* to give products in pure form 20 g (quant.) as whitish yellow solid materials. The sample was provided in next step without further purification. Data: R_f value 0.40 (hexane/EtOAc, 1:1); ¹H NMR (400 MHz, CDCl₃) 8.92 (d, J = 1.9 Hz, 1H, H-4), 8.79 (d, J = 1.9 Hz, 1H, H-5), 8.75 (d, J= 1.9 Hz, 1H, H-12), 8.57 (d, J = 1.8 Hz, 1H, H-13), 8.53 (d, J = 8.9 Hz, 1H, H-9), 8.52

(d, J = 8.8 Hz, 1H, H-8), 8.32 (d, J = 1.9 Hz, 1H, H-2), 8.07 (d, J = 8.6 Hz, 1H, H-16), 7.80 (dd, J = 8.9, 1.9 Hz, 1H, H-10), 7.79 (dd, J = 8.8, 1.9 Hz, 1H, H-7), 7.67 (dd, J = 8.6, 1.8 Hz, 1H, H-15), 1.51 (s, 9H, CH₃), 1.44 (s, 9H, CH₃) ppm; MS (DART-TOF) *m/z*: 640 [M]+; IR (neat): 2961, 2571 (OH), 1669 (C=O), 1472, 1395, 1291, 1257, 1089, 753 cm⁻¹; HRMS (DART-TOF) calcd. for C₃₅H₃₀⁷⁹Br₂O₂ [M]+: 640.0607, found: 640.0609.

For 7, 6,11-Dibromo-3,14-di-*tert*-butyldibenzo[g,p]chrysene-1-carbonyl chloride.



Under an argon atmosphere, to a solution of starting **6** (20 g, 31 mmol) in sulfurous dichloride (100 mL, 1.4 mol) at room temperature was added catalytic amounts of DMF (5 drops *via* syringe). After stirred at room temperature for 0.5 h, the mixture was concentrated *in vacuo* to give **7** in pure form as brown solid

materials. The sample was provided in the next step without further purification. Data: ¹H NMR (400 MHz, CDCl₃) 8.92 (d, J = 1.9 Hz, 1H, H-4), 8.81 (d, J = 1.8 Hz, 1H, H-5), 8.69 (d, J = 1.9 Hz, 1H, H-12), 8.58 (d, J = 1.9 Hz, 1H, H-13), 8.53 (d, J = 8.9 Hz, 1H, H-9), 8.52 (d, J = 8.8 Hz, 1H, H-8), 8.25 (d, J = 8.6 Hz, 1H, H-16), 7.99 (d, J = 1.9 Hz, 1H, H-2), 7.82 (dd, J = 8.9, 1.9 Hz, 1H, H-10), 7.79 (dd, J = 8.8, 1.8 Hz, 1H, H-7), 7.71 (dd, J = 8.6, 1.9 Hz, 1H, H-15), 1.50 (s, 9H, CH₃), 1.45 (s, 9H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) 172.0 (C=O), 151.5 (C-3), 149.5 (C-14), 135.5 (C-4c), 131.7 (C-7), 131.5 (C-10), 130.6 (C-8), 130.5 (C-9), 130.4 (C-8a), 130.0 (C-16), 129.9 (C-12c), 129.7 (C-1), 129.6 (C-8b), 129.5 (C-12a), 129.44 (C-16a), 129.37 (C-5), 129.0 (C-2), 126.5 (C-4b), 126.1 (C-12b), 126.0 (C-12), 125.7 (C-4a), 125.6 (C-16b), 125.4 (C-4), 125.1 (C-15), 125.0 (C-13), 121.6 (C-6), 121.4 (C-11), 35.6 (Q(CH₃)₃), 35.5 (Q(CH₃)₃), 31.6 (CH₃), 31.5 (CH₃) ppm; MS (DART-TOF) *m/z*: 623 [M-Cl]⁺; IR (neat): 2959, 1766 (C=O), 1591, 1470, 1395, 1362, 1205, 1038, 912, 798, 741, 714 cm⁻¹; HRMS (DART-TOF) calcd. for C₃₅H₂₉⁷⁹Br₂O [M-Cl]⁺: 623.0580, found: 623.0559.

For 8, 9,14-Dibromo-2,6-di-*tert*-butyl-4*H*-benzo[*p*]indeno[7,1,2-*ghi*]chrysen-4-one.



Under an argon atmosphere, to a solution of the starting **7** (21 g, 31 mmol) in dry CH_2Cl_2 (310 mL) at 0 °C was added AlCl₃ (4.2 g, 31 mmol). After stirred at 0 °C for 0.5 h, the reaction was quenched with H₂O (170 mL). The mixture was diluted with CHCl₃ (200 mL), and the aqueous phase was extracted with CHCl₃ (50 mL x 3), and the combined organic phases were

washed with brine (100 mL), dried over Na₂SO₄, and concentrated *in vacuo* to give crude products of 18 g as yellowish brown solid materials. Recrystallization from toluene (21.0 – 12.9 = 7.10 mL/g) yielded the first crop **8** of 9.9 g (50%) and the second 4.0 g (20%) as yellow solid materials. Data: R_f value 0.67 (hexane/EtOAc, 4:1); M.p. 327-329 °C; ¹H NMR (400 MHz, CDCl₃) 9.09 (d, J = 1.9 Hz, 2H, H-15), 8.72 (d, J = 0.8 Hz, 2H, H-3), 8.55 (d, J = 8.8 Hz, 2H, H-12), 8.02 (d, J = 0.8 Hz, 2H, H-1), 7.82 (dd, J = 8.8, 1.9 Hz, 2H, H-13), 1.51 (s, 18H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) 193.9 (C=O), 153.0 (C-2), 137.7 (C-3a), 133.1 (C-15c), 131.5 (C-3a¹), 130.5 (C-12), 129.9 (C-13), 128.2 (C-15b), 128.0 (C-1), 127.3 (C-11b), 124.9 (C-15), 123.9 (C-15a), 121.3 (C-3), 121.2 (C-14), 36.0 (Q(CH₃)), 31.6 (CH₃) ppm; MS (DART-TOFMS) *m/z*: 623 [MH] +; IR (neat): 2953, 1713 (C=O), 1453, 1362, 1200, 1092, 902, 799, 677 cm⁻¹; HRMS (DART-TOF) calcd. for C₃₅H₂₉7⁹Br₂O [MH]+: 623.0585, found: 623.0582; Anal. Calcd. for C₃₅H₂₈Br₂O; C, 67.32; H, 4.52. Found: C, 67.28; H, 4.58.

For 9, 2,6-Di-tert-butyl-4H-benzo[p]indeno[7,1,2-ghi]chrysen-4-one. Under a



nitrogen atmosphere, to a 50 mL two-neck flask charged with a solution of starting **8** (1.2 g, 2.0 mmol) in 2-butanol (20 mL) were added PPh₃ (63 mg, 0.24 mmol), and K_2CO_3 (830 mg, 6.0 mmol), and Pd(OAc)₂ (14 mg, 0.060 mmol). The reaction mixture was stirred at room temperature for 10 minutes. After stirred at 90 °C

for 14 h, the mixture was allowed to cool to ambient temperature. The mixture was

filtered through a pad of silica-gel and celite (CH₂Cl₂ only), and the mixture was transferred into a 300 mL separatory funnel, and washed with water (40 mL x 3) and brine (50 mL), and dried over Na₂SO₄, and concentrated *in vacuo* to give 970 mg of crude products as dark yellow solid materials. Purification by silica-gel column chromatography (hexane/ CH₂Cl₂, 2:1) afforded 820 mg of 9 as yellow solid materials in 88% yield. Data: Rf value 0.41 (hexane/toluene, 1:1); M.p. 321-323 °C; ¹H NMR (400 MHz, CDCl₃) 8.91 (dd, J = 7.5 Hz, 2.2 Hz, 2H, H-15), 8.80 (dd, J = 7.9 Hz, 1.9 Hz, 2H, H-12), 8.77 (d, J = 1.1 Hz, 2H, H-3), 7.99 (d, J = 1.1 Hz, 2H, H-1), 7.77 (ddd, J = 7.5 Hz, 7.0 Hz, 1.9 Hz, 2H, H-14), 7.73 (ddd, J = 7.9 Hz, 7.0 Hz, 2.2 Hz, 2H, H-13), 1.51 (s, 18H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) 194.3 (C=O), 152.2 (C-2), 137.4 (C-3a), 132.9 (C-3a1), 130.10 (C-12), 130.06 (C-15c), 128.2 (C-1), 127.7 (C-11b), 127.5 (C-13), 126.7 (C-14), 126.6 (C-3), 124.3 (C-15b), 123.3 (C-15), 120.5 (C-15a), 35.7 (<u>C</u>(CH₃)), 31.4 (CH₃) ppm; MS (DART-TOFMS) *m*/*z*: 467 [MH]+; IR (neat): 2951, 1713 (C=O), 1448, 1362, 1203, 894, 757, 738 cm⁻¹; HRMS (DART-TOF) calcd. for C₃₅H₃₁O: 467.2375 [MH]+, found: 467.2347; Anal. Calcd. for C₃₅H₃₀O: C, 90.09; H, 6.48. Found: C, 90.11; H, 6.54.

For 4, 4H-Benzo[p]indeno[7,1,2-ghi]chrysen-4-one. Under an argon atmosphere, to



a solution of the starting **9** (1.6 g, 3.4 mmol) in dry benzene (140 mL) was added AlCl₃ (9.1 g, 68 mmol). After stirred at 80 °C for 2 h, the reaction was quenched with H₂O (140 mL) at 0 °C. The aqueous layer was extracted with toluene (70 mL x 3), and the

combined organic phases were washed with brine (200 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to give 1.6 g of crude products. Purification by silica-gel column chromatography (hexane/CHCl₃, 1:2) yielded **4** in 1.6 g as orangish yellow solid materials (84%). Data: R_f value 0.45 (hexane/CH₂Cl₂, 1:2); M.p. 275-277 °C; ¹H NMR (400 MHz, CDCl₃) 8.90 (dd, J = 7.5, 1.4 Hz, 2H, H-15), 8.79 (dd, J = 7.5,

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1.4 Hz, 2H, H-12), 8.76 (d, J = 8.3 Hz, 2H, H-1), 7.87 (d, J = 6.9 Hz, 2H, H-3), 7.76 (ddd, J = 7.5, 6.9, 1.4 Hz, 2H, H-14), 7.72 (ddd, J = 7.5, 6.9, 1.4 Hz, 2H, H-13), 7.67 (dd, J = 8.3, 6.9 Hz, 2H, H-2) ppm; ¹³C NMR (100 MHz, CDCl₃) 194.0. (C=O), 139.8 (C-3a¹), 133.1 (C-3a), 132.7 (C-1), 130.7 (C-15c), 130.4 (C-11b), 129.2 (C-3), 128.3 (C-12), 127.9 (C-15b), 127.5 (C-13), 127.3 (C-14), 125.7 (C-15a), 123.9 (C-2), 122.5 (C-15) ppm; MS (DART-TOFMS) *m/z*: 355 [MH]+; IR (neat) 1702 (C=O), 1599, 1422, 1025, 914, 727, 714 cm⁻¹; HRMS (DART-TOF) calcd. for C₂₇H₁₅O: 355.1123 [MH]+, found: 355.1119; Anal. Calcd. for C₂₇H₁₄O: C, 91.50; H, 3.98. Found: C, 91.43; H, 3.97.

4) Synthesis of 1 (Scheme 5). For 1, 4,4'-(4*H*-benzo[*p*]indeno[7,1,2-*ghi*]chrysene-4,4 diyl)diphenol. Under an argon atmosphere, to a suspension of the starting ketone



(800 mg, 2.3 mmol) in phenol (1.0 mL, 23 mmol) at 80 °C (oil bath temp.) was added methanesulfonic acid (0.07 mL, 1.1 mmol). After stirred for 4 h, the reaction mixture was allowed to cool to ambient

temperature, and diluted with ethyl acetate (20 mL). The mixture was washed with brine (15 mL × 3), dried over Na₂SO₄, and concentrated *in vacuo* to give 2.2 g of crude products. The resulting sample was washed with hexane (180 mL) and dried *in vacuo* (100 °C, 1 h) to give 870 mg of the target molecules as whitish brown solid materials. Purification by short-plugged silica-gel column chromatography (toluene/EtOAc, 9:1) afforded 810 mg of the desired molecules in 69% yield as whitish yellow solid materials. Further purification by recrystallization from toluene (1000 - 841 = 159 mL, 106 mL/g) gave the first prisms of 404 mg (34%) as whitish yellow materials. Data: *R_t* value 0.38 (toluene/EtOAc, 4:1); M.p. > 350 °C; 1H NMR (400 MHz, CD₃CN) 9.03 (dd, *J* = 8.5, 1.7 Hz, 2H, H-15), 8.82 (dd, *J* = 8.5, 1.8 Hz, 2H, H-12), 8.68 (d, *J* = 8.2 Hz, 2H, H-1), 7.77-7.67 (m, 8H, H-2, H-3, H-13, H-14), 7.12 (dd, *J* = 8.7, 2.0 Hz, 4H, phenyl H-3), 6.86 (s, 2H, phenyl OH), 6.68 (dd, *J* = 8.7, 2.0 Hz, 4H, phenyl H-2) ppm; ¹³C NMR

(100 MHz, DMSO- d_6) 156.2 (phenyl C-1), 150.0 (phenyl C-4), 135.2 (C-12, C-2, two peaks are overlapped), 129.9 (C-13), 129.7 (C-14), 128.8 (phenyl C-3, phenyl C-5, two peaks are overlapped), 128.4 (C-3a), 128.1 (C-3a¹), 127.6 (C-1), 127.4 (C-3), 127.3 (C-15c), 125.2 (C-15), 125.0 (C-11b), 123.9 (C-15b), 122.9 (C-15a), 115.2 (phenyl C-2, phenyl C-6, two peaks are overlapped), 66.2 (C-4) ppm; MS (DART-TOFMS) *m/z*: 525 [MH]+; IR (neat): 3486 (OH), 3366 (OH), 3059, 1606, 1506, 1426, 1174, 827, 718, 560 cm⁻¹; HRMS (DART-TOFMS) calcd. for C₃₉H₂₅O₂: 525.1855 [MH]+, found: 525.1859; Anal. Calcd for C₃₉H₂₄O₂; C, 89.29; H, 4.61. Found: C, 89.47; H, 4.64.

3. Molecular packing structure of 4 with ORTEP drawings (Figure S1).



Figure S1. Molecular packing structure of **4** with ORTEP drawings with description of intramolecular distances; (a) top view, and (b) side view. The hydrogen atoms are omitted for clarity.

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4. Cartesian coordinates of optimized structures in DFT calculations for 1 (Table

S1). DFT Calculation: All calculations were conducted using the Gaussian 09, Revision E.01 suite of programs with default thresholds and algorism. Optimization was performed at the B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequency analysis was conducted with the optimized structures at the same level of theory to verify all stationary points as local minima (with no imaginary frequency).

Table S1. Cartesian Coordinates of Optimized Structures: Cartesian coordinates for **1**, optimized at the B3LYP/6-31G(d,p) level of theory.

		Coordinates (Angstroms)			
Center Number	Atomic Type	Х	Y	Z	
1	8	0.000002753	-0.000003576	-0.000010352	
2	1	0.000004596	-0.000000891	0.000008837	
3	8	-0.000003672	0.000003949	0.000002495	
4	1	0.000002809	0.000008253	-0.000001029	
5	6	0.000017819	0.000004587	0.000013042	
6	6	-0.000002903	0.000000685	0.000011068	
7	6	-0.000009141	0.000005223	-0.000010883	
8	1	0.000003324	0.000001316	0.000000501	
9	6	-0.000007495	0.000001043	-0.000014167	
10	6	-0.000005906	0.000013176	-0.00000313	
11	6	0.000011951	-0.00000854	0.00000873	
12	1	0.000001333	0.000003201	0.000007443	
13	6	-0.000003926	0.000000216	0.000007897	
14	6	0.000010319	-0.000017168	0.000008771	
15	6	0.00000211	0.000004532	0.000010577	
16	6	0.000002312	-0.0000031	0.000002471	
17	6	0.000004032	0.000013909	0.00000466	

18	1	-0.000007253	-0.000007063	-0.000003804
19	6	-0.000001852	0.000001523	-0.000000238
20	6	-0.000000953	-0.000016627	0.000008428
21	1	-0.000002971	0.000004115	-0.000002474
22	6	0.00000945	0.000009986	-0.000021791
23	6	0.000001862	0.000010485	-0.000042517
24	6	-0.000009117	-0.000006873	0.000001784
25	1	-0.000008809	0.00000029	-0.000008854
26	6	-0.000005211	-0.000013548	-0.000001484
27	1	0.000002507	0.000003078	0.000012152
28	6	-0.000002886	0.00000008	-0.000013344
29	6	0.000007455	0.000000175	0.000012558
30	6	0.000004745	0.000001871	-0.000014045
31	1	-0.000005047	-0.000000872	0.0000046
32	6	0.000000496	-0.000005297	-0.00001428
33	6	0.000001046	0.000003414	0.000020598
34	1	0.000005288	0.000000514	-0.000003751
35	6	-0.000015305	0.000004512	-0.00000429
36	1	0.000006312	0.000008209	0.000001264
37	6	0.000004825	-0.000003207	-0.000005044
38	1	-0.000006151	0.000001717	-0.000000993
39	6	0.000007773	0.000000434	0.000010922
40	6	-0.000010395	0.000006887	-0.000005548
41	1	0.000005369	-0.000002916	-0.000000755
42	6	-0.000000981	-0.000002148	0.000010508
43	1	0.00000644	0.000002364	-0.000003489
44	6	0.000006301	-0.000001214	0.000006268
45	1	-0.000014204	0.000003075	-0.000007254
46	6	0.000002274	-0.000002225	0.000002194
47	6	-0.000016742	-0.000028283	0.000007151
48	1	0.000003888	0.000000391	-0.000010939

49	6	-0.000011628	0.000011188	-0.000010939
50	1	0.000005996	-0.000004697	0.000006415
51	6	-0.00000254	-0.000002772	0.000000114
52	6	0.000005189	0.00001261	-0.000005183
53	1	-0.000001205	-0.000006762	0.000018878
54	6	0.000002152	0.000002971	0.000002373
55	1	0.000002496	-0.000004769	0.000014944
56	6	-0.000005019	-0.000000322	-0.000006367
57	1	-0.000001702	0.00000341	-0.000004872
58	6	-0.000002768	-0.000006581	0.000008697
59	1	-0.00000209	0.000005425	-0.00000974
60	6	0.000002245	-0.000005071	0.000004147
61	1	0.000002869	-0.000004961	-0.000010438
62	6	-0.000004504	0.000005162	0.000002598
63	1	0.000006814	-0.000003477	0.000004743
64	6	0.000003743	-0.000005912	0.000002495
65	1	0.00000148	0.00000353	-0.000008098

5. Refractive Index for each BPF and 1 (Figure S2)

(a)

Compound	wt% Concentration (DMSO)	1st	2nd	3rd	Average
BPF	5	1.5201	1.5200	1.5200	1.5200
	10	1.5288	1.5288	1.5288	1.5288
	15	1.5333	1.5335	1.5335	1.5334
1	10	1.5996	1.5995	1.5994	1.5995
	15	1.6057	1.6055	1.6053	1.6055
	20	1.6253	1.6252	1.6251	1.6252



Figure S2. Refractive index measurement: (a) data of refractive indices in several concentration wt% (DMSO) for BPF and **1**, and (b) calibration curves for the refractive indices of BPF (red line) and **1** (blue line), providing 1.64 for BPF and 1.83 for **1** in 100 wt%.



6. UV/Vis absorption and fluorescence spectra for 1 (Figure S3 and Table S2)

Figure S3. The normalized UV/Vis absorption and fluorescence spectra of hexane solution (red), THF solution (green), and CH₂Cl₂ solution (blue).

Solvent	λ1 _{Abs, max} (nm)	λ2 _{Abs, max} (nm)	λ3 _{Abs, max} (nm)	λ4 _{Abs, max} (nm)	λ1 _{em, max} (nm)	λ1 _{Excitation} (nm)	φ _{FL} (%)
Hexane	271	294	306	344	406	306	4.1
THF	274	-	304	345	408	304	9.2
CH ₂ Cl ₂	273	297	308	346	409	308	7.3

Table S2. Evaluation of UV/Vis absorption and optical properties for 1.

7. ¹H and ¹³C NMR spectra







Compound **2** (^{13}C NMR spectrum in CDCl₃).





Compound **5** (¹³C NMR spectrum in CDCl₃).



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Compound 4 (¹³C NMR spectrum in CDCl₃).







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