Supporting Information

Synthesis and Characterization of Charge-Transporting π-Stacked Polybenzofulvene Derivatives

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Synthesis. Merck silica gel 60 (230–400 mesh) was used for column chromatography. Merck TLC plates, silica gel 60 F_{254} were used for TLC. Melting points were determined in open capillaries in a Gallenkamp apparatus and are uncorrected. UV/vis spectra were recorded with a Perkin Elmer Lambda 40 spectrophotometers and the emission spectra were performed by means of a Perkin Elmer LS45 instrument. NMR spectra were recorded with a Bruker AC200, a Varian Mercury-300, a Bruker DRX-400 AVANCE, or a Bruker DRX-600 AVANCE spectrometer in the indicated solvents (TMS as internal standard): the values of the chemical shifts are expressed in ppm and the coupling constants (J) in Hz. An Agilent 1100 LC/ MSD operating with an electrospray source was used in mass spectrometry experiments.

Ethyl 2-(3,5-Dimethoxybenzyl)-3-oxo-3-phenylpropanoate (6a).

A mixture of ethyl benzoylacetate (1.2 mL, 6.93 mmol) in DMF (15 mL) with K_2CO_3 (2.9 g, 21 mmol), NaI (1.0 g, 6.77 mmol), and compound **5a** (1.26 g, 6.75 mmol) was stirred at room temperature for 18 h. The reaction mixture was then diluted with a saturated NH_4Cl solution and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate (8:2) as the eluent gave compound **6a** (2.22 g, yield 96%) as a pale yellow oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.07 (t, J = 7.4, 3H), 3.23 (d, J = 7.2, 2H), 3.65 (s, 6H), 4.05 (q, J = 6.9, 2H), 4.62 (t, J = 6.8, 1H), 6.24 (s, 1H), 6.34 (s, 2H), 7.38-7.53 (m, 3H), 7.92 (d, J = 8.2, 2H). MS (ESI): m/z 365 ($M + Na^+$).

Ethyl 3-Oxo-3-phenyl-2-(3,4,5-trimethoxybenzyl)propanoate (6b).

A mixture of ethyl benzoylacetate (1.2 mL, 6.93 mmol) in DMF (15 mL) with K_2CO_3 (2.9 g, 21 mmol), NaI (1.0 g, 6.77 mmol), and **5b** (1.5 g, 6.92 mmol) was stirred at room temperature for 4 h. The reaction mixture was then diluted with a saturated NH_4Cl solution and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and evaporated under reduced pressure.

Purification of the residue by flash chromatography with petroleum ether-ethyl acetate (6:4) as the eluent gave compound **6b** (2.04 g, yield 79%) as a white solid (mp 111-111.5 °C). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.12 (t, J = 6.8, 3H), 3.26 (d, J = 7.1, 2H), 3.77 (s, 9H), 4.10 (q, J = 7.2, 2H), 4.59 (t, J = 7.4, 1H), 6.39 (s, 2H), 7.46 (m, 3H), 7.93 (d, J = 8.6, 2H). MS (ESI): m/z 395 ($M + Na^+$).

Ethyl 4,6-Dimethoxy-3-phenyl-1*H*-indene-2-carboxylate (7a).

Compound **6a** (2.1 g, 6.13 mmol) was mixed with polyphosphoric acid by mechanical stirring at room temperature for 30 min. The reaction mixture was then diluted with water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate (1:1) as the eluent gave the expected indene derivative **7a** (1.84 g, yield 93%) as a pale yellow solid (mp 95 – 97 °C). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.02 (t, J = 7.2, 3H), 3.48 (s, 3H), 3.78 (s, 2H), 3.84 (s, 3H), 4.02 (q, J = 7.2, 2H), 6.32 (d, J = 1.8, 1H), 6.70 (d, J = 1.8, 1H), 7.31 (m, 5H). MS (ESI): m/z 347 ($M + Na^+$).

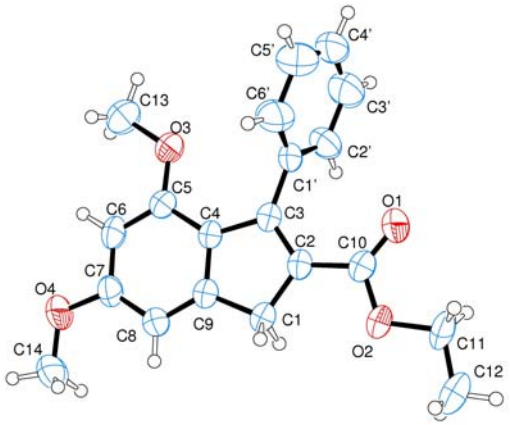

Figure 1 SI. Crystal structure of compound **7a**. Ellipsoids enclose 50% probability.

Ethyl 3-Phenyl-4,5,6-trimethoxy-1H-indene-2-carboxylate (7b).

A mixture of compound **6b** (1.6 g, 4.29 mmol) in sulfuric acid (2.0 mL) was stirred at room temperature for 30 min. The reaction mixture was diluted with ethanol (30 mL) and then with water (10 mL). The resulting mixture was extracted with ethyl acetate and the organic layer was dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography with petroleum ether-ethyl acetate (8:2) as the eluent gave the expected indene derivative **7b** (0.75 g, yield 49%) as a pale yellow solid (mp 96 – 98 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.02 (t, J = 7.1, 3H), 3.31 (s, 3H), 3.77 (s, 2H), 3.80 (s, 3H), 3.91 (s, 3H), 4.03 (q, J = 7.1, 2H), 6.89 (s, 1H), 7.37 (m, 5H). MS (ESI): m/z 355 ($M + H^+$).

Ethyl 4,6-Dimethoxy-1-oxo-3-phenyl-1*H*-indene-2-carboxylate (1a).

A mixture of compound **7a** (1.7 g, 5.24 mmol) and SeO_2 (8.6 g, 77.5 mmol) in 1,4-dioxane (20 mL) was heated at reflux for 4 h. After cooling to room temperature, a saturated solution of $NaHCO_3$ was added dropwise and the resulting mixture was extracted with ether. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography with petroleum ether-ethyl acetate (8:2) as eluent to obtain compound **1a** (1.25 g, yield 71%) as a purple solid. An analytical sample was obtained by recrystallization from ether (mp 122 – 123 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.04 (t, J = 7.1, 3H), 3.54 (s, 3H), 3.86 (s, 3H), 4.07 (q, J = 7.1, 2H), 6.39 (d, J = 2.0, 1H), 6.85 (d, J = 2.0, 1H), 7.39 (m, 5H). MS (ESI): m/z 361 ($M + Na^+$).

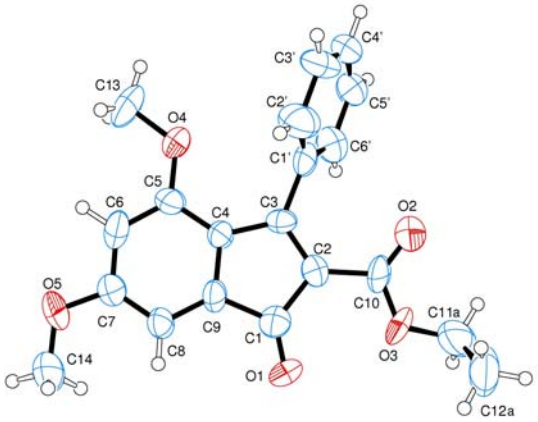

Figure 2 SI. Crystal structure of compound **1a**. Ellipsoids enclose 50% probability. The depicted ethyl group has site occupation factor of 0.62(3).

Ethyl 4,5,6-Trimethoxy-1-oxo-3-phenyl-1*H*-indene-2-carboxylate (1b).

A mixture of compound **7b** (1.0 g, 2.82 mmol) and SeO_2 (0.94 g, 8.47 mmol) in 1,4-dioxane (20 mL) was heated at reflux overnight. After cooling to room temperature, a saturated solution of $NaHCO_3$ was added dropwise and the resulting mixture was extracted with ether. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography with petroleum ether-ethyl acetate (8:2) as eluent to obtain compound **1b** (0.49 g, yield 47%) as a red solid. An analytical sample was obtained by recrystallization from ether (mp 110–111 °C). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.02 (t, J = 7.2, 3H), 3.32 (s, 3H), 3.83 (s, 3H), 3.91 (s, 3H), 4.07 (q, J = 7.2, 2H), 7.05 (s, 1H), 7.42 (m, 5H). MS (ESI): m/z 391 ($M + Na^+$).

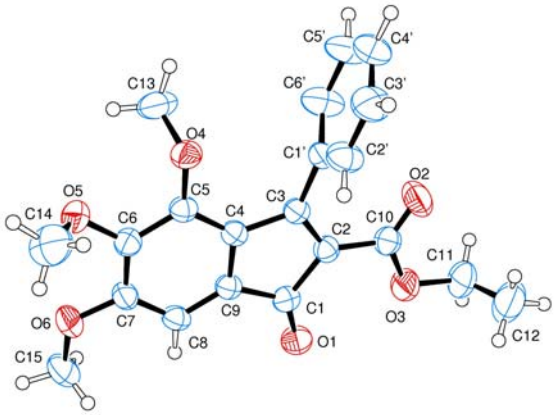

Figure 3 SI. Crystal structure of compound **1b**. Ellipsoids enclose 50% probability.

Ethyl 1-Hydroxy-4,6-dimethoxy-1-methyl-3-phenyl-1*H*-indene-2-carboxylate (2a).

To a mixture of indenone derivative **1a** (1.1 g, 3.25 mmol) in CH_2Cl_2 (30 mL), a solution (2M in THF) of $Al(CH_3)_3$ (3.3 mL, 6.6 mmol) was added and the resulting mixture was stirred at room temperature under nitrogen for 30 min. The excess of $Al(CH_3)_3$ was cautiously decomposed with a 30% NaOH solution until the gas evolution ceased. The mixture was filtered and the filtrate was dried over sodium sulfate and evaporated under reduced pressure. Purification of the residue with petroleum ether-ethyl acetate (1:1) as the eluent gave indenol derivative **2a** (0.75 g, yield 65%) as a yellow oil, which crystallized on standing (mp 98-100 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (t, *J* = 7.1, 3H), 1.72 (s, 3H), 3.46 (s, 3H), 3.77 (s, 1H), 3.87 (s, 3H), 4.01 (m, 2H), 6.31 (s, 1H), 6.77 (s, 1H), 7.31 (m, 5H). MS (ESI): m/z 377 ($M + Na^+$).

Ethyl 1-Hydroxy-4,5,6-trimethoxy-1-methyl-3-phenyl-1*H*-indene-2-carboxylate (2b).

To a mixture of indenone derivative **1b** (0.47 g, 1.28 mmol) in CH_2Cl_2 (30 mL), a solution (2M in THF) of $Al(CH_3)_3$ (1.3 mL, 2.6 mmol) was added and the resulting mixture was stirred at room temperature under nitrogen for 30 min. The excess of $Al(CH_3)_3$ was cautiously decomposed with a 30% NaOH solution until the gas evolution ceased. The mixture was filtered and the filtrate was dried over sodium sulfate and evaporated under reduced pressure. Purification of the residue with petroleum ether-ethyl acetate (8:2) as the eluent gave indenol derivative **2b** (0.33 g, yield 67%) as a yellow oil, which crystallized on standing (mp 85-87 °C). ^{1}H-NMR (200 MHz, $CDCl_3$): 0.92 (t, *J* = 7.3, 3H), 1.73 (s, 3H), 3.29 (s, 3H), 3.77 (s, 3H), 3.81 (s, 1H), 3.94 (s, 3H), 4.06 (m, 2H), 6.94 (s, 1H), 7.34 (m, 5H). MS (ESI): m/z 407 ($M + Na^+$).

Ethyl 4,6-Dimethoxy-1-methylene-3-phenyl-1*H*-indene-2-carboxylate (4,6-MO-BF3k).

A mixture of indenol derivative **2a** (0.10 g, 0.28 mmol) in $CHCl_3$ (200 mL) with a catalytic amount of *p*-toluenesulfonic acid monohydrate (PTSA) (0.010 g, 0.053 mmol) was heated at reflux for 3 h and then cooled to room temperature. The reaction mixture was washed with a saturated solution of $NaHCO_3$ and dried over sodium sulfate to afford a stock solution of monomer 4,6-MO-**BF3k**. An analytical sample of monomer 4,6-MO-**BF3k** was obtained by flash chromatography of the stock solution with $CDCl_3$ as the eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (t, J = 7.1, 3H), 3.50 (s, 3H), 3.88 (s, 3H), 4.01 (q, J = 7.1, 2H), 6.32 (s, 1H), 6.33 (d, J =2.0, 1H), 6.58 (s, 1H), 6.90 (d, J = 2.0, 1H), 7.31 (m, 5H). MS (ESI): m/z 359 ($M + Na^+$).

Ethyl 4,5,6-Trimethoxy-1-methylene-3-phenyl-1*H*-indene-2-carboxylate (4,5,6-MO-BF3k).

A mixture of indenol derivative **2b** (0.16 g, 0.42 mmol) in $CHCl_3$ (20 mL) with a catalytic amount of PTSA (0.016 g, 0.084 mmol) was heated at reflux until disappearance of starting **2b** from the chromatogram (10-15 min.) The reaction mixture was then washed with a saturated solution of $NaHCO_3$ and dried over sodium sulfate to afford a stock solution of monomer 4,5,6-MO-**BF3k**. An analytical sample of monomer 4,5,6-MO-**BF3k** was obtained by flash chromatography of the stock solution using $CDCl_3$ as the eluent. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.91 (t, J = 7.0, 3H), 3.30 (s, 3H), 3.80 (s, 3H), 3.88-4.02 (m, 5H), 6.26 (s, 1H), 6.57 (s, 1H), 7.07 (s, 1H), 7.34 (m, 5H). MS (ESI): m/z 389 ($M + Na^+$).

Poly(Ethyl 4,6-Dimethoxy-1-methylene-3-phenyl-1*H*-indene-2-carboxylate) (poly-4,6-MO-BF3k).

The stock solution of benzofulvene monomer 4,6-MO-**BF3k** in chloroform was concentrated under reduced pressure to give a viscous oil, which was dissolved into chloroform (10 mL/mmol of monomer) and newly evaporated (the dissolution/evaporation procedure was repeated three times). The final residue was dissolved into a small amount of CH_2Cl_2 and precipitated with ethanol to give

poly-4,6-MO-**BF3k** as a white electrostatic solid (0.048 g, yield from **2a** 51%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.1-1.0 (br m, 3H), 2.4-4.5 (br m, 10H), 5.2-7.6 (br m, 7H).

Poly(Ethyl 4,5,6-Trimethoxy-1-methylene-3-phenyl-1*H*-indene-2-carboxylate) (poly-4,5,6-MO-BF3k).

The solution of benzofulvene monomer 4,5,6-MO-**BF3k** into chloroform was concentrated under reduced pressure to give a viscous oil, which was dissolved into chloroform (10 mL/mmol of monomer) and newly evaporated (the dissolution/evaporation procedure was repeated three times). The final residue was dissolved in a small amount of CH_2Cl_2 and precipitate with ethanol to give poly-4,5,6-MO-**BF3k** as a white electrostatic solid (0.065 g, yield from **2b** 42%). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.1-1.0 (br m, 3H), 2.1-4.9 (br m, 13H), 5.7-7.9 (br m, 6H).

Dimers 3a and 4a.

The mixture of dimers **3a** and **4a** was isolated by flash chromatography (chloroform as the eluent) from the stock solution of benzofulvene monomer 4,6-MO-**BF3k**. The mixture was crystallized from *n*-hexane-ether-methanol by slow evaporation to obtain a mixture of crystals showing different shapes and morphological parameters. The dimers were identified by submitting different crystals to X-ray diffraction studies.

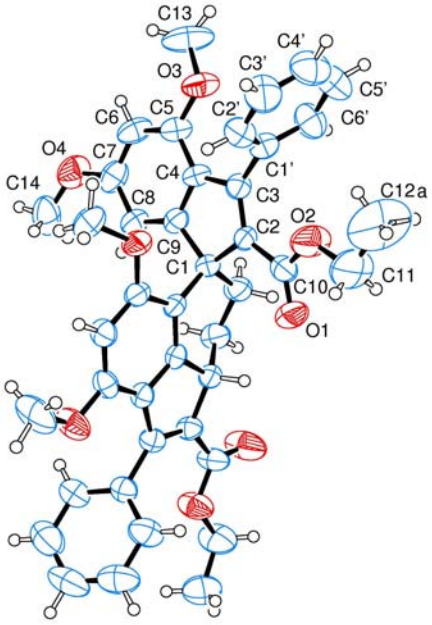

Figure 4 SI. Crystal structure of dimer **3a**. Ellipsoids enclose 50% probability. Partial labeling is given for clarity's sake. The depicted C(12a)H_3 group has a site occupation factor of 0.51(1).

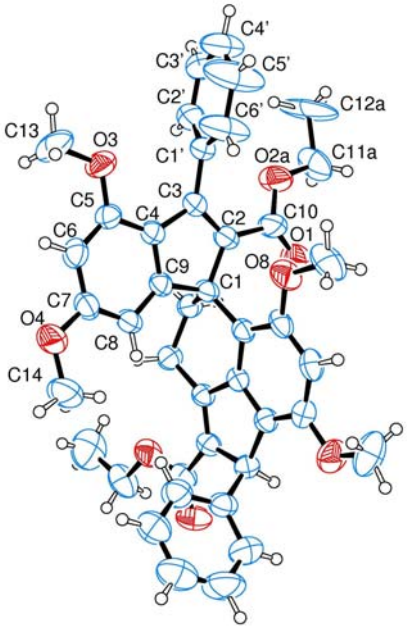

Figure 5 SI. Crystal structure of compound **4a×CH_3OH**. Ellipsoids enclose 50% probability. The methanol molecule and partial labeling are omitted for clarity's sake. The depicted ethoxy group O(2a)-C(12a) has a site occupation factor of 0.59(1).

Dimers 3b and 4b.

The mixture of dimers **3b** and **4b** was isolated by flash chromatography (chloroform as the eluent) from the stock solution of benzofulvene monomer 4,5,6-MO-**BF3k**. The mixture was crystallized from *n*-hexane-ether by slow evaporation to obtain a mixture of crystals of different shapes. The dimers were identified by submitting different crystals to X-ray diffraction studies.

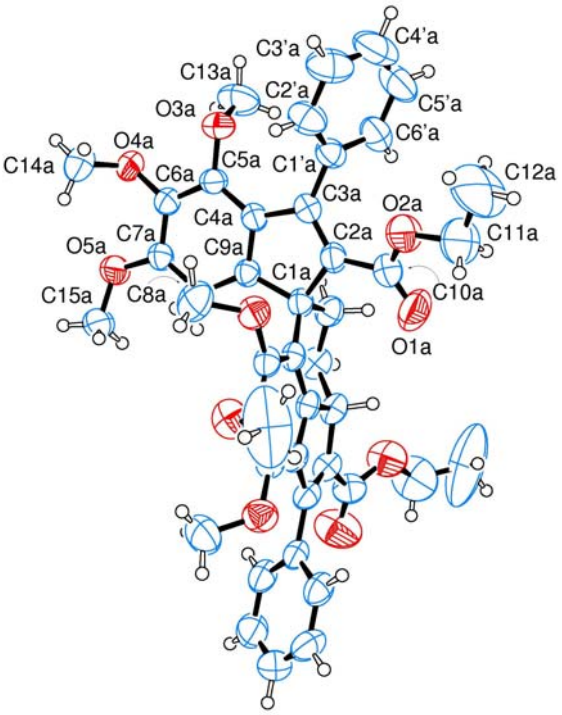

Figure 6 SI. Crystal structure of dimer **3b**. Ellipsoids enclose 50% probability. Only one molecule of the asymmetric unit is shown and partial labeling is given for clarity's sake.

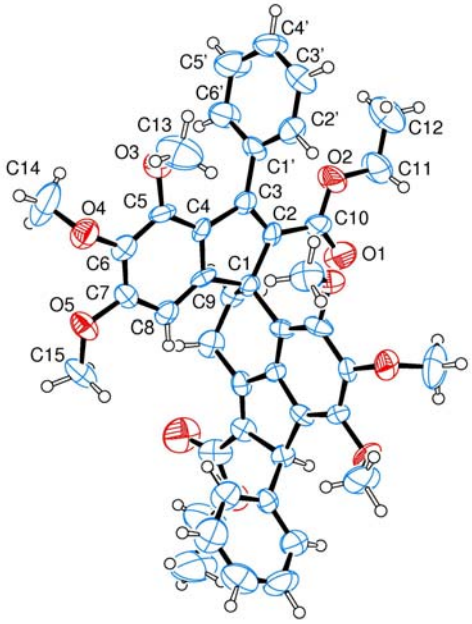

Figure 7 SI. Crystal structure of dimer **4b**. Ellipsoids enclose 50% probability. Partial labeling is given for clarity's sake.