Supporting information

Synthesis of interface derivatives

Materials

All chemical reagents and dehydrated solvents were commercially available and used without further purification. Analytical thin layer chromatography was performed on commercial Merck plates coated with silica gel $60F_{254}$. Silica gel used for chromatography was Aldrich silica gel 60 and Merck silica gel 60.

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and/or DMSO-d_6 solutions on a JEOL AL300/BZ spectrometer at 300 and 75.5 MHz, respectively. Chemical shifts in $CDCl_3$ are reported in ppm downfield from TMS, and coupling constants are in hertz. ESI-MS spectra were recorded on an Applied Biosystems Mariner V 4.0 mass spectrometer. Elemental analyses were performed on Sumika Chemical Analysis Service (SCAS).

Synthesis of tripod molecule (tripodal derivative)

tris(4-methylphenyl)methanol 4. To a THF solution (40 ml) of 4,4'-dimethylbenzophenone **3** (10.666 g, 50.724 mmol) was added dropwise a 1.0 M THF solution of *p*-tolylmagnesium bromide (100 ml, 0.1 mol) during 0.5 h at rt under nitrogen, and the resulting solution was refluxed for 4 days. After cooling to rt, 1 N HCl aq. was added to hydrolysis. The organic layer was extracted with chloroform (200 ml). The extract was washed with 200 ml of water, dried with $MgSO_4$, filtered, and concentrated to give residue, which was passed through silica gel using chloroform as an eluent following recrystallization from hexane to give **4** (11.759 g, 76.7%) as white crystals.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.33 (s, 9H, C*H*$_3$), 2.69 (s, 1H, O*H*), 7.09 (d, *J* 8.4 Hz, 6H, arom. H), 7.15 (d, *J* 8.1 Hz, 6H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 20.10, 81.57, 127.75, 128.52, 136.70, 144.28.

tris(4-methylphenyl)methylchloride 5.[1] A tris(4-methylphenyl)methanol **4** (10.134 g; 33.510 mmol) was refluxed in acetyl chloride (70 ml) for over night under nitrogen. After removal of acetyl chloride, the residue was recrystallized from hexane to give **5** (10.089 g, 93.8%) as white crystals.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.35 (s, 9H, C*H*$_3$), 7.09 (d, *J* 8.7 Hz, 6H, arom. H), 7.13 (d, *J* 8.1 Hz, 6H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 21.01, 81.66, 128.31, 129.56, 137.43, 142.66.

4-[tris(4'-methylphenyl)methyl]aniline 6.[2] A mixture of tris(4-methylphenyl)methylchloride **5** (2.927 g, 9.122 mmol) and aniline (45 ml) was heated under reflux for over night under nitrogen. The purple-colored mixture was precipitated in 200 ml of 10% HCl aq., and the crude product was collected by filtration, dissolved in 150 ml of dichloromethane. It was washed with 200 ml of potassium carbonate in water, washed with 200 ml of water, dried with $MgSO_4$, filtered, and concentrated to give residue, which was passed through silica gel using chloroform as an eluent following recrystallization from dichloromethane-hexane to give **6** (3.039 g, 88.2%) as crystals.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.30 (s, 9H, C*H*$_3$), 3.57 (br, 2H, N*H*$_2$), 6.55 (d, *J* 8.7 Hz, 2H, arom. H), 6.96 (d, *J* 8.7 Hz, 2H, arom. H), 7.02 (d, *J* 8.4 Hz, 6H, arom. H), 7.08 (d, *J* 8.4 Hz, 6H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 20.88, 63.15, 114.10, 127.98, 130.88, 131.91, 134.99, 137.51, 143.83, 144.565.

4-dimethyltriazenylphenyl-tris(4'-methylphenyl)methane 7.[3] To a flask charged with 4-[tris(4'-methylphenyl)methyl]aniline **6** (6.028 g, 15.967 mmol) was added 12 N HCl aq. (4.3 ml), THF (36 ml), and water (67 ml). To this mixture, cooled with an ice bath, and stirred, aqueous solution of sodium nitride (1.472 g, 21.335 mmol) in water (13 ml) was added dropwise. The reaction mixture was allowed to stir at rt for 0.5 h until a homogeneous solution was obtained, transferred to a solution containing potassium carbonate (11.426 g, 82.674 mmol), diethylamine (3.0 ml), THF (145 ml), and water (28 ml) cooled in an ice bath. Then the reaction mixture was stirred for 0.5 h at rt. After more added water (100 ml), it was extracted with chloroform (100 ml). The organic layer was dried with $MgSO_4$, filtered, and concentrated to give residue, which was purified by column chromatography on silica gel using chloroform-hexane (2: 3 *v/v*) as eluent, and dried to give **7** (6.525 g, 88.5%) as a powder.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 1.23 (t, *J* 7.2 Hz, 6H, CH_3), 2.30 (s, 9H, ArCH_3), 3.72 (q, *J* 7.1 Hz, 4H, CH_2), 7.02 (d, *J* 8.4 Hz, 6H, arom. H), 7.11 (d, *J* 8.4 Hz, 6H, arom. H), 7.16 (d, *J* 8.7 Hz, 2H, arom. H), 7.28 (d, *J* 8.7 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 20.88, 63.59, 119.19, 128.03, 130.92, 131.51, 135.05, 144.05, 144.35, 148.76.

4-iodophenyl-tris(4'-methylphenyl)methane 8.[3] A mixture of 4-dimethyltriazenylphenyl-tris(4'-methylphenyl)methane **7** (6.525 g, 14.134 mmol), iodine (10.090 g, 39.754 mmol), and methyl iodide (55 ml) was heated with 80 °C for 4 h. After removal of methyl iodide, the residue was extracted with chloroform (100 ml) and water (100 ml). The organic layer was dried with $MgSO_4$, filtered, and concentrated to give residue, which was purified by column chromatography on silica gel using chloroform-hexane (1: 4 *v/v*) as

eluent following recrystallization from dichloromethane-methanol to give **8** (3.982 g, 57.7%) as white crystals.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.31 (s, 9H, C*H*$_3$), 6.965 (d, *J* 8.7 Hz, 2H, arom. H), 7.015-7.08 (m, 12H, arom. H), 7.53 (d, *J* 8.7 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 20.89, 63.67, 91.50, 128.25, 130.77, 133.10, 135.45, 136.42, 143.60, 147.25.

tris[4-(acetylthiomethyl)phenyl]-4'-iodophenylmethane 9.[4] A mixture of 4-iodophenyl-tris(4'-methylphenyl)methane **8** (2.499 g, 5.117 mmol), NBS (3.010 g, 19.912 mmol), and AIBN (0.253 g, 1.535 mmol) was refluxed in carbon tetrachloride (30 ml) for 1 day under nitrogen. After cooling to rt, it was filtered using chloroform, and the filtrate was concentrated. The resulting residue and potassium thioacetate (3.508 g, 30.712 mmol) were refluxed in dry THF (40 ml) for 4 h under nitrogen. The solution was concentrated under reduced pressure, and the resulting residue was dissolved in 100 ml of chloroform. It was washed with 100 ml of saturated sodium thiosulfate, 100 ml of water, dried with $MgSO_4$, and filtered to give residue, which was purified by column chromatography on silica gel using chloroform as an eluent to give **9** (1.199 g, 33.0%) as a viscosity solid.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.35 (s, 9H, C*H*$_3$), 4.08 (s, 6H, ArC*H*$_2$S), 6.91 (d, *J* 8.7 Hz, 2H, arom. H), 7.06 (d, *J* 8.4 Hz, 6H, arom. H), 7.14 (d, *J* 8.4 Hz, 6H, arom. H), 7.54 (d, *J* 8.4 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 30.34, 32.87, 63.945, 91.835, 128.06, 131.03, 132.95, 135.33, 136.63, 145.04, 146.34, 195.11.

methyl 4-(trimethylsilylethynyl)benzoate 11. A mixture of 4-iodobenzoate **10** (10.022 g, 38.245 mmol), $Pd(PPh_3)_2Cl_2$ (0.538 g, 0.766 mmol), and CuI (0.294 g, 1.544 mmol) was stirred

in dry THF (40 ml) and triethylamine (20 ml) at rt for 1 h under nitrogen. To the solution was added trimethylsilylacetylene (10.6 ml), and the resulting solution was stirred at rt for 1 day. The solution was filtered using THF, and the filtrate was concentrated under reduced pressure. The resulting residue was dissolved in hexane, and filtered to remove insoluble materials. The filtrate was concentrated to give residue, which was purified by column chromatography on silica gel using chloroform as an eluent to give **11** (8.571 g, 96.5%) as a solid.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 0.26 (s, 9H, SiCH_3), 3.91 (s, 3H, OCH_3), 7.515 (d, *J* 8.1 Hz, 2H, arom. H), 7.97 (d, *J* 8.4 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) –0.18, 52.21, 97.68, 104.04, 127.25, 129.36, 129.67, 131.86, 166.50.

methyl 4-ethynylbenzoate 12. A mixture of methyl 4-(trimethylsilylethynyl)benzoate **11** (6.778 g, 29.171 mmol) and potassium carbonate (0.649 g, 4.696 mmol) was stirred in dichloromethane (15 ml) and methanol (40 ml) at rt for 1 h under nitrogen. The solution was filtered, and the filtrate was concentrated to give residue, which was passed through silica gel using chloroform as an eluent to give **12** (4.324 g, 92.5%) as a solid.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 3.23 (s, 1H, alkyne-H), 3.92 (s, 3H, OCH_3), 7.55 (d, *J* 8.4 Hz, 2H, arom. H), 7.99 (d, *J* 8.1 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 52.26, 80.025, 82.77, 126.72, 129.43, 130.11, 132.05, 166.40.

tris[4-(acetylthiomethyl)phenyl]-[4'-(4"-methoxycarbonylphenyl)ethynylphenyl]-methane 1b. A mixture of tris[4-(acetylthiomethyl)phenyl]-4'-iodophenylmethane **9** (1.115 g, 1.569 mmol), methyl 4-ethynylbenzoate **12** (0.307 g, 1.917 mmol), $Pd(PPh_3)_2Cl_2$ (0.050 g, 0.07123 mmol), and CuI (0.043 g, 0.2257 mmol) was stirred in dry THF (20 ml) at rt for 3 days

in the presence of triethylamine (10 ml) under nitrogen. The solution was filtered using THF to remove insoluble materials, and the filtrate was concentrated under reduced pressure. The resulting residue was extracted with chloroform (50 ml) and saturated sodium thiosulfate (150 ml) twice. The organic layer was dried with $MgSO_4$, filtered, and concentrated to give residue, which was purified by column chromatography on silica gel using chloroform as an eluent following recrystallization from dichloromethane-hexane to give **1b** (0.534 g, 45.8%) as fluffy crystals like cotton.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.36 (s, 9H, C*H*$_3$CO), 3.925 (s, 3H, OC*H*$_3$), 4.09 (s, 6H, ArC*H*$_2$S), 7.08-7.19 (m, 14H, arom. H), 7.40 (d, *J* 8.7 Hz, 2H, arom. H), 7.56 (d, *J* 8.7 Hz, 2H, arom. H), 8.01 (d, *J* 8.7 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 30.35, 32.87, 52.23, 64.21, 88.73, 92.14, 120.25, 127.96, 128.065, 129.38, 129.48, 130.925, 130.97, 131.09, 131.47, 135.29, 145.12, 147.33, 166.545, 195.16.

ESI-MS: *m/z* 765.2 ([M+Na]$^+$).

Anal. Calcd. for $C_{44}H_{38}S_3O_5$: C, 71.13; H, 5.155%. Found: C, 71.22; H, 5.14%.

4-(4'-carboxyphenyl)ethynylphenyl-tris[4"-(mercaptomethyl)phenyl]methane 1a. To THF (5 ml)-ethanol (5 ml) solution of tris[4-(acetylthiomethyl)phenyl]-[4'-(4"-

methoxycarbonylphenyl)ethynylphenyl]-methane **1b** (0.110 g, 0.148 mmol) was added sodium hydroxide (0.247 g, 6.175 mmol) in 2 ml of water, and the resulting solution was stirred for 5 h at rt. Then 50 ml of water was added, and the resulting solution was hydrolysis by conc. HCl aq. to adjust pH 1 to give precipitate, which was collected by filtration and dried.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.88 (t, *J* 7.8 Hz, 3H, S*H*), 3.69 (d, *J* 7.8 Hz, 6H, ArC*H*$_2$S), 7.09 (d, *J* 7.8 Hz, 6H, arom. H), 7.21 (d, *J* 8.4 Hz, 2H, arom. H), 7.27 (d, *J* 8.1 Hz, 6H,

arom. H), 7.51 (d, *J* 8.1 Hz, 2H, arom. H), 7.625 (d, *J* 8.1 Hz, 2H, arom. H), 7.95 (d, *J* 8.1 Hz, 2H, arom. H), 13.14 (br, 1H, COO*H*).

Synthesis of reference molecule (single point contact derivative)

4-acetylthiomethyl-iodobenzene 14. A mixture of 4-iodobenzylbromide **13** (5.721 g, 19.267 mmol) and potassium thioacetate (2.450 g, 21.452 mmol) was refluxed in dry THF (60 ml) for 4 h under nitrogen. The solution was filtered using chloroform, and the filtrate was concentrated to give residue, which was purified by column chromatography on silica gel using chloroform-hexane (1: 1 *v/v*) as eluent to give **14** (5.224 g, 92.8%) as solid.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.345 (s, 3H, CH_3), 4.04 (s, 2H, ArCH_2S), 7.035 (d, *J* 8.4 Hz, 2H, arom. H), 7.61 (d, *J* 8.4 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 30.31, 32.87, 92.66, 130.76, 137.45, 137.67, 194.84.

methyl 4-(4”-acetylthiomethylphenyl)ethynylbenzoate 2b. A mixture of 4-acetylthiomethyl-iodobenzene **14** (2.000 g, 6.846 mmol), methyl 4-ethynylbenzoate **12** (1.321 g, 8.247 mmol), $Pd(PPh_3)_2Cl_2$ (0.109 g, 0.1552 mmol), and CuI (0.083 g, 0.4358 mmol) was stirred in dry THF (40 ml) at rt for 1 day in the presence of triethylamine (10 ml) under nitrogen. The solution was filtered using THF to remove insoluble materials, and the filtrate was concentrated under reduced pressure. The resulting residue was extracted with chloroform (100 ml) and sat. sodium thiosulfate (200 ml). The organic layer was dried with $MgSO_4$, filtered, and concentrated to give residue, which was purified by column chromatography on silica gel using chloroform as an eluent following recrystallization from dichloromethane-methanol to give **2b** (2.103 g, 94.7%) as a powder.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) 2.36 (s, 3H, C*H*$_3$CO), 3.92 (s, 3H, OC*H*$_3$), 4.12 (s, 2H, ArC*H*$_2$S), 7.28 (d, *J* 8.4 Hz, 2H, arom. H), 7.47 (d, *J* 8.1 Hz, 2H, arom. H), 7.57 (d, *J* 8.4 Hz, 2H, arom. H), 8.01 (d, *J* 8.7 Hz, 2H, arom. H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 30.30, 33.20, 52.21, 88.835, 92.02, 121.60, 127.89, 128.91, 129.425, 129.47, 131.46, 131.91, 138.49, 166.50, 194.85.

ESI-MS: *m/z* 347.1 ($[M+Na]^+$), 671.1 ($[2M+Na]^+$).

Anal. Calcd. for $C_{19}H_{16}SO_3$: C, 70.35; H, 4.97%. Found: C, 70.46; H, 4.89%.

4-(4'-mercaptomethylphenyl)ethynylbenzoic acid 2a. To THF (5 ml)-ethanol (5 ml) solution of methyl 4-(4"-acetylthiomethylphenyl)ethynylbenzoate **2b** (0.101 g, 0.311 mmol) was added 2 ml of 1.0 M aqueous solution of sodium hydroxide, and the resulting solution was stirred for 5 h at rt. Then 50 ml of water was added, and the resulting solution was hydrolysis by conc. HCl aq. to adjust pH 1 to give precipitate, which was collected by filtration and dried.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.95 (t, *J* 7.8 Hz, 1H, S*H*), 3.76 (d, *J* 7.8 Hz, 2H, ArC*H*$_2$S), 7.40 (d, *J* 8.1 Hz, 2H, arom. H), 7.53 (d, *J* 7.8 Hz, 2H, arom. H), 7.65 (d, *J* 8.1 Hz, 2H, arom. H), 7.96 (d, *J* 7.8 Hz, 2H, arom. H), 13.12 (br, 1H, COO*H*).

Reference lists for supporting information

S1. Davis, G. L.; Hey, D. Y.; Williams, G. H. *J. Chem. Soc.* **1956**,4397-4408.

S2. Heim, C.; Affeld, A.; Nieger, M.; Vögtle, F. *Helv. Chim. Acta* **1999**, *82*, 746-759.

S3. cf) Zhu, Z.; Moore, J. S. *J. Org. Chem.* **2000**, *65*, 116-123.

S4. cf) Hirayama, D.; Takimiya, K.; Aso, Y.; Otsubo, T.; Hasobe, T.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Sakata, Y. *J. Am. Chem. Soc.* **2002**, *124*, 532-533.