Supporting information on

Cationic two-photon absorption chromophores with double- and triple-bonds-cores in symmetric/asymmetric arrangements

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1. Synthetic procedure and characterization of Compounds 1 and 4 and the intermediates.

Route. The “half MPPBT”-compound 4 was also obtained from 5, by the quarternization reaction (Scheme 1). The ethyne-core compound 1 was synthesized by the Sonogashira reaction between 5 and 6, followed by the quarternization reaction. Compounds 5 and 6 were prepared by the reported method.[1]

Scheme 1. Synthetic routes of 1 and 4.

1-Ethynyl-2,5-dimethoxy-4-{2-[4-(N-methyl)pyridin-1-iumyl]ethenyl}benzene triflate (4). To a stirred solution of 5 (5.8 g, 21.8 mmol) in dichloromethane (70 ml) was added methyl trifluoromethanesulfonate (4.65 g, 28.3 mmol) at room temperature, and it was then stirred for 1.5 h. After the solvent was evaporated under reduced pressure, the residue was recrystallized from a mixture solvent of methanol (150 ml) and water (150 ml) to give an orange solid. Yield, 4.2 g (45 %); Mp 211 °C; Td > 220 °C; $^1$H NMR(400 MHz, DMSO-d$_6$, ppm): δ 8.82 (d, 2H, pyridyl), 8.20 (d, 2H, pyridyl), 8.01 (d, 2H, Py-CH=CH-Ph), 7.61 (d, 2H, Py-CH=CH-Ph), 7.41 (s, 2H, phenyl), 7.19 (s, 2H, phenyl), 4.48 (s, 1H, -C≡CH), 4.25 (s, 3H, Py-CH$_3$), 3.87 (s, 3H, -OCH$_3$), 3.86 (s, 3H, -OCH$_3$). Anal. Calcd for C$_{19}$H$_{18}$NO$_5$F$_3$S: C, 53.14; H, 4.23; N, 3.26; F, 7.47. Found: C, 53.01; H, 4.22; N, 3.23; F, 7.43.

1,2-Bis{4-[2,5-dimethoxy-4-(4-pyridyl)vinyl]phenyl}ethyne (7). Compound 6 (0.85g, 2.64 mmol) was dissolved in a mixture solvent of triethylamine (100 ml) and THF (50 ml). To this solution were added Cu(I)I (0.0251 g, 0.132 mmol), PdCl$_2$(Ph$_3$P)$_3$ (0.092 g, 0.132 mmol), Ph$_3$P (0.0692, 0.264 mmol), and slowly added dropwise 5 (0.70 g, 2.64 mmmol) in a mixture solvent of triethylamine (100 ml) and THF (50 ml) under nitrogen. The solution was stirred and refluxed for 24 h and the solvent was evaporated under reduced pressure. To the residue was added 10 % acetic acid and the solution was neutralized with aqueous potassium carbonate solution. The solution was extracted with chloroform,
washed with water and dried over MgSO₄. After the solvent was evaporated under reduced pressure, the residue was recrystallized from chloroform (100 ml) and ethyl acetate (50 ml) to give an orange solid. Yield, 0.38 g (29%); Td > 220 °C; ¹H NMR(400 MHz, DMSO-d₆, ppm): δ 8.58 (d, 4H, pyridyl), 7.68 (d, 2H, Py-CH=CH-Ph), 7.62 (d, 4H, pyridyl), 7.54 (d, 2H, phenyl), 7.40 (d, 2H, Py-CH=CH-Ph), 7.22 (s, 2H, phenyl) 3.96 (s, 6H, -OCH₃), 3.92 (s, 6H, -OCH₃). ¹³C NMR(100 MHz, DMSO-d₆, ppm): δ 154.4, 151.4, 150.1, 150.0, 144.6, 128.0, 127.2, 120.8, 120.7, 116.5, 111.3 (styrylpyridyl), 91.3 (C≡C), 56.9, 56.7 (-OCH₃). TOF-mass: m/z 505.42 (M⁺). Anal. Calcd for C₃₂H₂₈N₂O₄: C, 76.17; H, 5.59; N, 5.55. Found: C, 75.8; H, 5.39; N, 5.21.

1,2-Bis[2,5-dimethoxy-4-[4-(N-methyl)pyridin-1-iumylviny]phenyl]ethyne triflate (1). To a stirred solution of 7 (0.1 g, 0.19 mmol) in dichloromethane (3.5 ml) was added methyl trifluoromethanesulphonate (0.078 g, 0.47 mmol), and it was then stirred at room temperature for 12 h. After the solvent was evaporated under reduced pressure, the residue was recrystallized from methanol (50 ml) to give a red solid. Yield, 0.10 g (64%). Td > 350 °C; ¹H NMR(400 MHz, DMSO-d₆, ppm): δ 8.82 (d, 4H, pyridyl), 8.30 (d, 4H, pyridyl), 8.13 (d, 2H, Py-CH=CH-Ph), 7.64 (d, 2H, Py-CH=CH-Ph), 7.46 (d, 2H, phenyl), 7.20 (s, 2H, phenyl), 4.24 (s, 6H, Py-CH₃), 3.91 (s, 6H, -OCH₃), 3.90 (s, 6H, -OCH₃). ¹³C NMR(100 MHz, DMSO-d₆, ppm): δ 153.9, 152.5, 151.9, 145.2, 134.4, 125.1, 125.0, 123.6, 116.1, 114.4, 110.7 (styrylpyridyl), 119.1 (q, CF₃SO₂, J = 320.8 Hz), 92.2 (C≡C), 56.3 (-OCH₃), 47.0 (Py-CH₃). Anal. Calcd for C₃₆H₃₄F₆N₂O₁₀S₂: C, 51.92; H, 4.12; N, 3.36; F, 13.69. Found: C, 51.63; H, 3.98; N, 3.51; F, 13.20.

2. Synthetic procedure and characterization of Compound 2 and the intermediates.

**Route.** The butadiene-core compound 2 was obtained by the Heck reaction between 1,4-phenylbutadiene derivative 13 and 4-vinylpyridine followed by the quaternization reaction (Scheme 2). Compound 13 was synthesized by the Wittig-Horner reaction of 11 and 12. Compound 11 was synthesized by the Vilsmeier-Haak reaction of 10 that was synthesized by additional reaction between Wittig regnant and aldehyde compound 9. Compound 9 was synthesized by N,N-dimethylsulfoxide (DMSO) oxidation reaction of the starting compound 8. Compounds 8 and 12 were prepared by the reported method. [1]
1-bromo-2,5-dimethoxy-benzaldehyde (9). To a solution of sodium hydrogen carbonate (42.0 g, 0.50 mmol) in DMSO (350 ml) was added 8 (26.6 g, 0.10 mmol) at room temperature and it was then stirred for 20 h at 115 °C. After the solvent was removed under reduced pressure, the residue was extracted with dichloromethane, washed with water and dried over MgSO\textsubscript{4}. After the solvent evaporated under reduced pressure, the dark oil was purified on a column of silica gel using chloroform as the eluent. After the solution evaporated under reduced pressure, the residue was recrystallized from a mixture solvent of hexane (500 ml) and ethylacetate (100 ml) to give an orange yellow crystal. Yield, 18.2 g (74.3 %); Mp 350 °C; Td > 170 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm): δ 10.4 (s, 1H, aldehyde), 7.34 (s, 1H, phenyl), 7.27 (s, 1H, phenyl), 3.89 (s, 6H, -OCH\textsubscript{3}). IR (KBr): 1678 (υC=O) cm\textsuperscript{-1}. Anal. Calcd for C\textsubscript{19}H\textsubscript{19}FbrO\textsubscript{3}: C, 44.11; H, 3.70; Br, 32.60; O, 19.59. Found: C, 44.32; H, 3.61, Br, 32.30.

1-bromo-2,5-dimethoxy-4-[2-(formyl)vinyl]benzene (11). Methyltriphenylphosphonium bromide (21.9 g, 61.2 mmol) was dissolved in THF (100 ml) containing t-BuOK (8.24 g, 73.4 mmol). To this solution was added THF (100 ml) solution of 9 (15.0 g, 61.2 mmol) and the solution was stirred at room temperature for 1.5 h. After the solvent evaporated under reduced pressure, the residue was extracted with chloroform, washed with water and dried over MgSO\textsubscript{4}. After the solvent was evaporated under reduced pressure, the crude product of 1-bromo-2,5-dimethoxy-4-vinylbenzene (10) was obtained and this used next step without further purification. (Distillation (86-100 °C /2 Torr) and crystallization from hexane (20 ml) can give the pure product of 10 as a white crystal, but little yield would be
anticipated because the degradation reaction occurs during distillation.) Phosphoryl chloride (13.2 g, 86.0 mmol) was added dropwise to DMF (34.3 g, 469.2 mmol) solution below 10 °C. To this solution were added the crude product (10) in DMF (10 ml) under 10 °C, and it was then stirred for 1 h at room temperature, and it was next heated at 80 °C for 1 h. After the solution was cooled, sodium acetate (81.6 g, 994.5 mmol) in water (200 ml) was added and the solution heated at 75 °C for 15 min. After the solvent was re-cooled, the solution was extracted with ether, washed with water and dried over MgSO4. After the solvent was evaporated under reduced pressure, the residue was purified on a column of silica gel using chloroform/hexane(2/1) as an eluent. After the solution was evaporated under reduced pressure, the residue was recrystallized from methanol (50 ml) to give a yellow crystal. Yield, 18.2 g (74.3 %); Mp 150 °C; Td > 210 °C; 1H NMR (400 MHz, CDCl3, ppm): δ 9.70 (d, 1H, aldehyde), 7.78 (d, 1H, Ph-CH=CH-C-CHO), 7.27 (s, 2H, phenyl), 7.17 (s, 2H, phenyl), 6.76 (q, 1H, Ph-CH=CH-C-CHO), 3.89 (s, 6H, OCH3). 13C NMR (100 MHz, CDCl3, ppm): δ 194.2 (aldehyde), 152.7, 150.3, 146.8, 129.2, 122.6, 117.1, 116.2, 111.0 (aromatic-C), 56.8, 56.3 (-OCH3). IR (KBr): 1693 (υC=O) cm\(^{-1}\). Anal. Calcd for C11H11BrO3: C, 48.73; H, 4.09; Br, 29.47. Found: C, 48.33; H, 4.11; Br, 29.22.

1,4-bis(2,5-dimethoxy-4-bromo)butadiene (13). Compound 12 (21.9 g, 61.2 mmol) was dissolved in THF (30 ml) containing t-BuOK (0.671 g, 5.98 mmol). To this solution was added THF (30 ml) solution of 11 (0.90 g, 3.32 mmol) and it was then stirred for 1 h under nitrogen. After the solvent was evaporated under reduced pressure, the residue gave a dark yellow powder. The powder was recrystallized from a mixture solvent of ethylacetate (75 ml) and chloroform (75 ml) to give a yellow crystal. Yield, 1.05 g (65.3 %); Mp 240 °C; Td > 330 °C; 1H NMR (400 MHz, DMSO-d6, ppm): δ 7.29 (s, 4H, phenyl), 7.18 (s, 4H, phenyl), 7.15 (d, 2H, butadinyll), 6.92 (d, 2H, butadinyll), 3.85, 3.81 (s, 6H, -OCH3). Anal. Calcd for C20H20Br2O4: C, 49.61; H, 4.16; Br, 33.01. Found: C, 48.78; H, 4.10; Br, 34.23.

1,4-bis[2,5-dimethoxy-4-[2-(4-pyridyl)ethenyl]phenyl]butadiene (14). Compound 13 (0.80 g, 1.65 mmmol) were dissolved in a mixture solvent of triethylamine (130 ml) and acetonitrile (260 ml). To this solution was added (o-tol)3P (1.01 g, 3.30 mmol), 4-vinylpyridine (382.2 mg, 3.64 mmol) and Pd(OAc)2 (74.3 mg, 3.31 mmol) and it was then stirred and refluxed for 24 h under nitrogen. After the solvent was evaporated under reduced pressure, the residue was extracted with chloroform (50 ml) provided with the Soxhlet extractor. After the solvent evaporated under reduced pressure, the brown powder was recrystallized from THF to give a brown crystal. Yield, 0.14 g (15.9 %); Td > 172 °C; 1H NMR (400 MHz, DMSO-d6, ppm): δ 8.58 (d, 4H, pyridyl), 7.72 (d, 2H, ethenyl), 7.66 (d, 4H, pyridyl), 7.40 (d, 2H, ethenyl), 7.34, 7.35 (s, 2H, phenyl), 7.28, 7.04 (d, 2H, butadinyll). The elemental analysis of
this compound did not agreed with calculated values because this compound has strong adsorbed activity to the organic solvent.

1,4-Bis(2,5-dimethoxy-4-[2-[4-(N-methyl)pyridinium]ethenyl]phenyl)butadiene triflate (2). To a stirred solution of 14 (40.0 mg, 0.075 mmol) in dichloromethane (50 ml) was added methyl trifluoromethanesulfonate (30.9 mg, 0.188 mmol), and it was then stirred at room temperature for 1 h. After the solvent was evaporated under reduced pressure, the residue was recrystallized from methanol (30 ml) to give a red solid. Yield, 10 mg (15.5%); Td > 380 °C; $^1$H NMR (400MHz, DMSO-d$_6$, ppm): δ 8.78 (d, 4H, pyridyl), 8.17 (d, 4H, pyridyl), 8.04 (d, 2H, ethenyl), 7.57 (d, 2H, ethenyl), 7.43 (d, 2H, butadiynyl), 7.41 (d, 2H, phenyl), 7.39 (s, 2H, phenyl), 7.20 (d, 2H, butadiynyl), 4.23 (s, 6H, methyl), 3.95 (s, 6H, -OCH$_3$), 3.89 (s, 6H, -OCH$_3$). $^{13}$C NMR (100MHz, DMSO-d$_6$, ppm): δ 152.7, 150.7, 145.0, 134.9, 132.5, 129.3, 126.9, 123.6, 123.5, 123.3, 113.8, 110.8, 108.7 (styrylpyridyl, butadiynyl), 120.7 (q, CF$_3$SO$_3$, J = 322.1 Hz), 56.2 (-OCH$_3$), 46.8 (Py-CH$_3$). Anal. Calcd for C$_{38}$H$_{38}$F$_6$N$_2$O$_{10}$: C, 53.02; H, 4.45; N, 3.25; F, 13.24. Found: C, 52.80; H, 4.48; N, 3.37; F, 13.20.

3. Synthetic procedure and characterization of Compound 3 and the intermediates.

**Route.** The asymmetric butadiyne-core compound 3 was synthesized by the Cadiot-Chodkiewicz coupling between 15 and 16, followed by the quaternization reaction (Scheme 3). Compound 15 was prepared from 5 by bromination. Meanwhile, 16 was prepared from 12 by the Wittig-Horner reaction, followed by the Sonogashira reaction (Scheme 4). Compounds 5 and 12 were prepared by the reported method [1] as mentioned above.

![Scheme 3. Synthetic route of 3.](image-url)
1-Bromoethynyl-2,5-dimethoxy-4-(4-pyridyl)vinylbenzene (15). To NaOH (2.38 g, 59.6 mmol), water (50 ml) and THF (50 ml) and the mixture was cooled to 0 °C. To this cooled solution, was added dropwise Br<sub>2</sub> (2.38 g, 14.9 mmol), and slowly added dropwise 5 (0.79 g, 2.98 mmol) in THF (50 ml). The solution was stirred at 0 °C for 6 h and poured into iced water (650 ml) after the reaction. Yellow residue was collected by filtration under reduced pressure and immediately stored in a freezer. The residue 15 is used for the next step without further purification because it easily decomposes at room temperature. Yield, 0.82 g (79.9 %).

1-[2,5-dimethoxy-4-(4-diethylaminophenyl)vinylphenyl]-4-[2,5-dimethoxy-4-(4-pyridine)vinylphenyl]butadiyne (17). To ethylamine (40 ml), were added 97% hydroxylammonium chloride (12.5 mg, 0.18 mmol) and then Cu(I)Cl (5.90 mg, 0.06 mmol) under nitrogen. To this solution, were slowly added dropwise 16 (0.20 g, 0.60 mmol) in THF (20 ml) and then 15 (0.21 g, 0.60 mmol) in THF (20 ml) and stirred for 1h. Then the solvent was evaporated under reduced pressure. To the residue, was added acetic acid (20ml) and the solution was neutralized with aqueous sodium carbonate solution (600ml). The solution was extracted with chloroform, washed with aqueous sodium carbonate solution and then water, dried over MgSO<sub>4</sub>, and filtrated. After the solvent was evaporated from the filtrate under reduced pressure, the residue was purified on a column of silica gel using a 9:1 mixture of dichloromethane-acetone as the eluent and then recrystallized from the 1:1 mixture of ethanol-chloroform (40ml) to give red powder 17. Yield, 0.165 g (46.0 %).

1-[2,5-dimethoxy-4-(4-diethylaminophenyl)vinylphenyl]-4-[2,5-dimethoxy-4-(4-pyridinium)vinylphenyl]butadiyne triflate (3). To cooled dichloromethane below 0 °C with ice bath, was added 17 (335 mg, 0.56 mmol). To this solution, was added methyl trifluoromethanesulfonate (1.84 g, 11.2 mmol), and stirred for 1 h cooled with ice bath, to turn the solution from orange into red.
solvent was evaporated from the red solution under reduced pressure. The residue was recrystallized from the methanol-water (3:2) mixture (200ml) to give a red powder. Yield, 0.12 g (28.1 %). 

$^1$H NMR(400MHz, DMSO, ppm): δ 8.83 (d, 2H, pyridyl), 8.21 (d, 2H, pyridyl), 8.02 (d, 1H, ethenyl), 7.65 (d, 1H, ethenyl), 7.45 (s, 1H, phenyl), 7.38 (d, 2H, phenyl), 7.30 (s, 1H, phenyl), 7.29 (s, 1H, phenyl), 7.29 (d, 1H, ethenyl), 7.12 (s, 1H, phenyl), 7.10 (d, 1H, ethenyl), 6.66 (d, 2H, phenyl), 4.24 (s, 3H, methyl), 3.91 (s, 6H, methoxy), 3.89 (s, 6H, methoxy), 3.81 (q, 4H, -N-C$_2$H$_5$-CH$_3$), 1.09 (t, 6H, -N-CH$_2$-C$_3$H$_3$).

$^{13}$C NMR(100MHz, DMSO, ppm): δ 155.8, 155.2, 152.3, 151.7, 149.8, 147.4, 144.9, 134.2, 134.1, 131.5, 130.1, 127.8, 125.9, 125.3, 123.5, 116.7, 116.2, 112.6, 111.4, 110.7, 108.2, 107.3, 81.4, 79.8, 79.3, 77.6, 56.3, 56.1, 46.7, 43.4, 12.2. Elemental Anal. Calcd for C$_{41}$H$_{41}$F$_3$N$_2$O$_7$S$_1$N$_2$: C, 64.55; H, 5.42; N, 3.67; F, 7.47 Found: C, 64.40; H, 5.31; N, 3.57 ; F, 7.44 %.

1-Bromo-2,5-dimethoxy-4-(4-diethylaminophenyl)vinylbenzene (18). To t-BuOH (120ml), was dissolved t-BuOK (6.60 g, 58.9 mmol) at 50 ºC under nitrogen. To this solution, were added 12 (11.5 g, 31.3 mmol) and then dropwise 4-(diethylamino)benzaldehyde (6.66 g, 37.6 mmol) in t-BuOH (100 ml) and was refluxed at 50 ºC for 2h. Then the solvent was evaporated under reduced pressure to give yellow solid. To the yellow residue, was added water. This solution was extracted with dichloromethane, dried over MgSO$_4$, and filtrated. After the solvent was evaporated from the filtrate under reduced pressure, the residue was purified on a column of silica gel using chloroform as the eluent, and then recrystallized from hexane to give a yellowish green needle crystal 18. Yield, 6.56g (53.7 %).

1-(4-Diethylaminophenyl)vinyl-2,5-dimethoxy-4-trimethylsilylethynylbenzene (19). To a mixture of diethylamine (100 ml) and THF (100 ml), was dissolved 18 (11.3g, 29.0 mmol) and washed with nitrogen. To this solution, were added trimethylsilylacethylene (4.27 g, 43.5 mmol), then PPh$_3$ (0.51 g, 1.94 mmol), Cu(I)I (0.37 g, 1.94 mmol), and (Ph$_3$P)$_2$PdCl$_2$ catalyst (0.68 g, 0.97 mmol) and refluxed at 50 ºC for 20 h. After the reflux, the solution was filtrated and the solvent was evaporated under reduced pressure to give brown solid. To the brown residue, was added water and the solution was extracted with dichloromethane, dried over MgSO$_4$, and filtrated. After the solvent was evaporated from the filtrate under reduced pressure, the residue was purified on a column of silica gel using a 1:1 mixture of dichloromethane-hexane to give yellowish orange solid 19. This compound was used for the next step without characterization because the compound is strongly coupled to solvent. Yield, 10.0 g (84.7 %).
1-(4-Diethylaminophenyl)vinyl-2,5-dimethoxy-4-ethynylbenzene (16). To a mixture of methanol (100 ml) and THF (100 ml), was dissolved 19 (2.50 g, 6.13 mmol) and washed with nitrogen. To this solution, was added dropwise 85 % KOH (0.59 g, 9.20 mmol) in water (30 ml) and refluxed at 80 °C for 2 h. The salt was removed by filtration and the solvent was evaporated from the filtrate under reduced pressure to give orange solid. This orange residue was dissolved in dichloromethane. The solution was washed with water, extracted with dichloromethane, dried over MgSO₄, and filtrated. After the solvent was evaporated under reduced pressure, the residue was purified on a column of silica gel using a 3:2 mixture of dichloromethane-hexane to give reddish brown solid. The solid was further purified by recrystalization from ethanol (200 ml) to give orange solid 16. Yield, 1.65 g (80.2 %). ¹H NMR(400MHz, CDCl₃, ppm): δ 7.42 (d, 2H, phenyl), 7.18 (d, 2H, phenyl), 4.02 (m, 4H, O-CH₂-CH₃), 3.08 (d, 2H, Ph-CH₂-P), 1.23 (t, 6H, O-CH₂-CH₃).

4. References