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Supporting information for

Third- and High- Order Nonlinear Optical Properties of an Intramolecular Charge-Transfer Compound

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1. Synthesis of (TCNQ)₂OPV₃.

2I-OPV₃ (180 mg, 0.2 mmol, synthesized followed our previously reported procedures¹), 4-(dimethylamino)phenylacetylene (87 mg, 0.6 mmol), and a catalytic amount of CuI and PPh₃ were dissolved in a mixture of 20 mL of dry THF and 30 mL of redistilled triethylamine. Bis(triphenyl phosphine) palladium(II) chloride was added under nitrogen atmosphere and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The residue was loaded onto a silica gel column and eluted with dichloromethane to get the crude product of alkynyl-containing OPV₃ after the solvent was removed under reduced pressure. The crude product was used for the next reaction, because it was not stable enough for further purification. To the achieved dichloromethane solution of the crude product was added TCNQ (143 mg, 0.7 mmol), and the solution was stirred at room temperature for 1 h. After removing the solvent, the residue was loaded onto a silica gel column and eluted with dichloromethane. This afforded 121 mg of the final product as a deep brown solid. The total yield of the two steps was 45 %. Mp: 238.5 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 0.87 (t, 6H, J = 3.2 Hz), 1.20-1.28 (m, 32H), 1.47-1.53 (m, 4H), 1.86-1.88 (m, 4H), 3.14 (s, 12H), 4.04 (t, 4H, J = 6.5 Hz), 6.75-6.78 (m, 4H), 6.96-6.99 (m, 2H), 7.08-7.11 (m, 3H), 7.15-7.17 (m, 3H), 7.26-7.31 (m, 6H), 7.49-7.52 (m, 2H), 7.57-7.62 (m, 6H), 7.68-7.70 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 14.15, 22.68, 26.15, 29.33, 29.46, 29.58, 29.62, 29.63, 31.89, 40.18, 69.36, 71.27, 85.51, 110.58, 112.50, 112.61, 114.80, 123.70, 124.76, 125.19, 126.87, 127.27, 127.84, 129.63, 130.38, 131.63, 133.23, 134.43, 134.54, 135.82, 137.52, 143.49, 151.46, 152.31, 152.89, 154.14, 171.53. MALDI-TOF: m/z calcd for C90H92N10O2 1344.7, found 1344.9. Elemental analysis calcd (%) for C₉₀H₉₂N₁₀O₂: C, 80.32; H, 6.89; N, 10.41. Found: C, 79.96; H, 6.97; N, 10.54.



Scheme S1. Synthesis route to (TCNQ)₂OPV₃.

2. Transmittance in CH₂Cl₂.

The sample was dissolved in dichloromethane (CH₂Cl₂) with the concentration of 8×10^{-5} M. Fig.S2 show the transmittance spectrum of (TCNQ)₂OPV₃ in CH₂Cl₂.



Figure S1. The transmittance spectrum of (TCNQ)₂OPV₃ in CH₂Cl₂.

3. Schematic of the 4f coherent imaging system.

We developed 4f coherent imaging system by replacing the traditional one. The reference facula was used in the nonlinear acquisition instead of the main facula in the linear acquisition as the incident beam to fit the main facula in the nonlinear acquisition. This new system is not propitious to measure films materials with surface in homogeneities because the reference facula does not include the imperfect information of the materials.



Scheme S2. (a) Schematic of the developed 4f coherent imaging system (the part of expanding the laser beam from the OPG is not drawn in the figure). The nonlinear material (NL) is located in the focal plane. A, aperture with phase object; L_1 - L_4 , lenses; M_1 , M_2 , mirrors; BS1, BS2, beam splitters; tf, neutral filter. (b) Schematic of the circular aperture with phase object at the entry of the system.

4. NLO Measurement of the Solvent.

A series of experimental measurements at different peak-on-axis intensities from 3.26 to 23.3 GW/cm² were performed. Fig.S1a-b show the experimental main facula, reference facula of nonlinear image and their corresponding fluence distribution at x=300.



Figure S2. (a) The experimental main facula of nonlinear image and its fluence distribution at x=300. (b) The reference facula of nonlinear image and its fluence distribution at x=300. The comparison between the experimental nonlinear image and the calculated nonlinear image shows a very good agreement between experimental result and numerical simulation.