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Electronic supporting information

Charge-transfer complex versus σ-complex between TiO_2 and bis(dicyanomethylene) electron acceptors

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Here, we describe the synthesis methods of 1,4-TCNAQ and TCNTQ.

1,4-TCNAQ

To a solution of 1,4-naphthoquinone (158 mg, 1.0 mmol) and malononitrile (198 mg, 3.0 mmol) in dry CH_2C1_2 (100 ml), 14% $TiCl_4$ (3.0 mmol) in CH_2C1_2 (3 ml) was added at 273 K under argon atmosphere. Then pyridine (0.48ml, 6.0 mmol) was added dropwise to the mixture solution. The solution was refluxed for 17 hours. The reaction mixture was cooled to room temperature, washed with water (3 x 200ml) and extracted with CH_2C1_2 (250ml). The product was purified by column chromatography (silica gel, CH_2C1_2), giving a yellow solid (30.7 mg, yield 12%). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ/ppm 7.6 (singlet, 2 H), 7.8-7.9 (quartet, 2 H), 8.7-8.8 (quartet, 2 H); FAB-Mass (M^+) m/z found 254, calc. 254.06.

TCNTQ[1]

2,5-Dibromothiophene (0.42 g, 1.74 mmol), tetracyanoethylene oxide (1.00 g, 6.94 mmol) and 1,3-dibromopropane (20 ml) were stirred with N_2 bubbling at room temperature for 30 minutes. The reaction mixture was heated at 150 ºC for 2 hours and cooled to room temperature. The precipitate was purified by column chromatography, giving a yellow solid (0.13 g, 35.7 %). Mp: 178-179 ºC; APCI-MS: m/z = 209[M^-]; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67 (2H, singlet); IR(KBr): ν/cm^{-1} 3104, 2226, 1542.

Reference

1. K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, A. Kawamoto, J. Tanaka, *Bull. Chem. Soc. Jpn*. 1989, **62**, 1547.