Supplementary Material (ESI) for Chemical Communications

Supporting Information

Cross-conjugated Poly(p-Phenylene)-Aided Supramolecular Self-Organization of Fullerene Nanocrystallites

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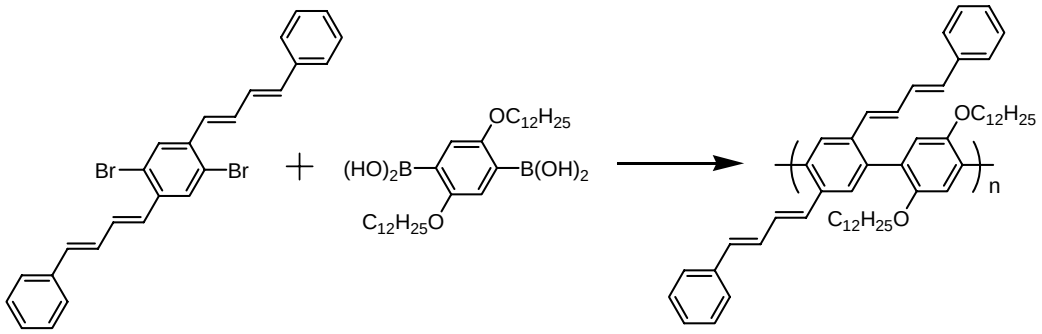
S1: Synthetic details of 2-dimensional (2D) orthogonally conjugated polymer.

1,4-Dibromo-2,5-bis-(4-phenyl-buta-1,3-dienyl)-benzene. A mixture of 1,4-dibromo-2,5-bis(bromomethyl)benzene (2 g, 4.8 mmol) and triethylphosphine (3.3 mL, 19.2 mmol) was refluxed for 6 hr and the excess triethylphosphine was removed under reduced pressure. The obtained ylid **(3)** was desolved in DMF (25 mL) and mixed with potassium *t*-butoxide (1.8 g, 19.2 mmol) and cinnamaldehyde (3.6 mL, 28.8 mmol). The mixture was stirred overnight at 50 ^{o}C, poured into water, filtered and the crude solid was recrystalized from MeOH, giving a yellow product with 75% yield. ^{1}HNMR (THF-d_8, δ ppm): 7.57-7.70 (m, 6H central Ar-H, terminal Ar-H), 7.30 (t, J = 7.5 Hz, 4H terminal Ar-H), 7.18 (t, J = 7.2 Hz, 2H, on terminal Ar-H), 6.90-6.96 (m, 4H, diene-H), 6.85 (d, J = 15.1 Hz, 2H, diene-H), 6.78 (d, J = 15.3 Hz, 2H, diene-H). ^{13}C NMR (THF-d_8, δ ppm): 138.1, 136.0, 134.1, 130.8, (Ar-C), 129.8, 129.3, 128.6, 128.0, 127.4, 126.9, 126.5, (Ar-C and diene-C). FTIR (KBr, cm^{-1}): 3022, 2924, 1753, 1610, 1458, 1446, 1365, 1053, 983, 887, 856, 821, 746, 684, 503. Elemental analysis: C: 63.44, H: 4.10, Br 32.47. Found: C: 63.04, H: 4.41, Br 32.16.

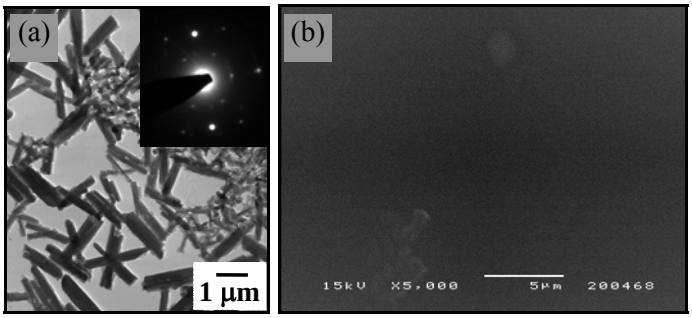
2,5-bis(dodecyloxy)phenyldiboronic acid: This was synthesized following literature (*Macromolecules* **2001**, *34*, 6255)

Poly (2,5-bis-(4-phenyl-buta-1,3-dienyl)-1,4-phenylene-*alt*-(2,5-bisdodecyloxy)-1,4-phenylene): 2,5-bis(dodecyloxy)phenyldiboronic acid (0.41g, 2.34 mmol) and 1,4-dibromo-2,5-bis(phenylbuta-1,3-dienyl)benzene (1g, 2.34 mmol) were dissolved in 30 mL THF. K_2CO_3 solution (2 M, 20 mL) was added to the mixture followed by

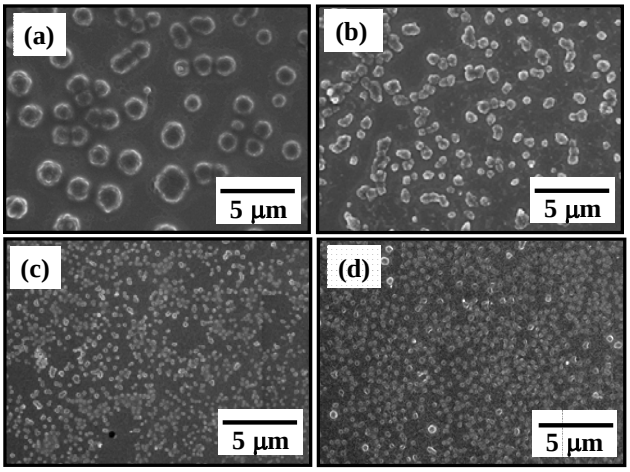
tetrakis(triphenylphosphino) palladium (0) (3 mol %) as catalyst and cetyltrimethyl ammonium bromide (30 mol %) as phase transfer agent. The mixture was stirred at 70 ^{o}C for 3 days, concentrated and precipitated twice from methanol and the crude product was further purified by filtration through silica gel using dichloromethane (DCM). ^{1}H NMR ($CDCl_3$, δ ppm): 7.58-7.73 (b, 8H, central Ar-H, terminal Ar-H, OAr-H), 7.29 (b, 4H, terminal Ar-H), 7.18 (b, 2H, terminal Ar-H), 6.93 (b, 6H, diene-H), 6.69 (b, 2H, diene-H), 3.90 (b ArOC**H$_2$**CH_2), 1.80 (b, $ArOCH_2C$**H$_2$**), 1.24 (b, (C**H$_2$**)$_3CH_3$), 0.88(b, C**H$_3$**). ^{13}C NMR ($CDCl_3$, δ ppm): 151.9, 140.7, (OAr-C), 138.0, 136.1, 133.6, 132.4, 130.5, 130.1, (Ar-C and OAr-C), 129.3, 128.5, 127.5, 126.2, 125.4, 118.2, (Ar-C, OAr-C and diene-C), 68.4, 31.8, 29.6, 27.2, 25.7, 22.5, 14.7, (Alk-C). FTIR (KBr, cm^{-1}): 3025, 2922, 2852, 1729, 1592, 1484, 1468, 1378, 1261, 1214, 1028, 990, 868, 803, 784, 721, 690, 618, 506. Elemental analysis: C: 86.3, H: 9.54. Found: C: 85.71, H: 9.89.



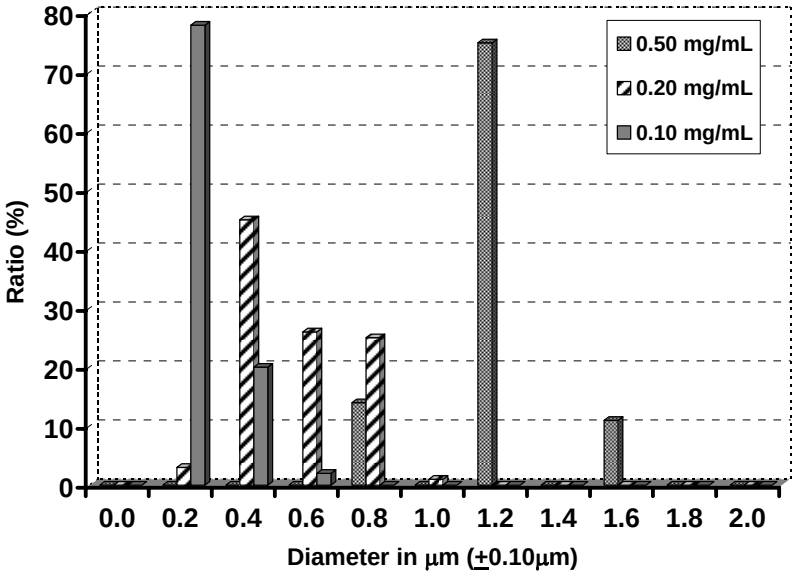
S2: (a) TEM micrographs with electron diffraction insets of C_{60} and (b) SEM micrographs of featureless C_{12}-xPPP film



S3: SEM images of C_{60}:C_{12}-xPPP 1:1 blend in toluene (a) spincoated at 100 rpm, (b) spincoated at 200 rpm, (c) spincoated at 500 rpm and (d) spincoated at 1000 rpm



S4: Size distribution of nanocrystallites prepared from solutions of different concentrations.



S5: UV absorbance of fullerene, C_{12}-xPPP and blend.