

Electronic Supplementary Information (ESI)

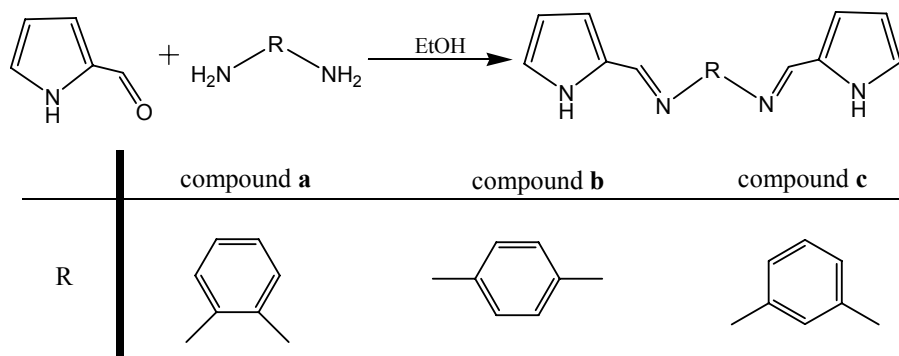
Distinct Nanostructures from Isomeric Molecules of Bis (pyrrol-2-ylmethyleneamine) benzenes: Effects of Molecular Structures on Nanostructural Morphologies

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Experimental section

General. All starting materials were purchased from Aldrich and used without further purification and solvents were disposed according to standard methods before using. Melting points were determined with a Yanaco MP-500 micro-melting point apparatus and are uncorrected. Samples for C, H, and N analyses were dried under vacuum and the analysis was performed with a Carlo Erba-1106 instrument. The ESI-MS measurements were carried out with a Bruker APEX II instrument. ¹H NMR spectra were recorded with a Bruker Avance dpx 400 MHz instrument using TMS as internal standard. The SEM records with a field emission scanning electron microscope (FESEM, JSM-6700F, JEOL) operating at an accelerating voltage of 3 kV. The TEM image and SAED pattern record with a transmission electron microscope (TEM, JOEL JEM-2010 operated at 200 kV). X-ray diffraction (XRD) measurements were performed by using a Rigaku X-Ray Diffractometer (D/max-2400) with an X-ray source of CuK α ($\lambda=1.5406 \text{ \AA}$) at 40 kV and 120 mA, at a scan rate of 0.028 (2 θ) per 0.12 s. The Raman spectra were recorded in the backscattering geometry by using a Renishaw-2000 Raman spectrometer with the 514.5 nm line of an Ar ion laser as the excitation source. The UV/Vis spectra were recorded in a Perkin Elmer lambda 35 UV/Vis spectrometer.

Synthesis of compound a, b, and c.



Diamine was added with stirring at room temperature to a solution of 2-carboxaldehydepyrrole in ethanol under nitrogen atmosphere. The reaction mixture was stirred overnight and a yellow precipitate formed. The solid was filtered off, washed with cold ethanol and dried in vacuum, then purified by column chromatography in neutral alumina with n-hexane/ethyl acetate/triethyl amine (v/v/v, 80/19/1) as eluent.

Compound a of 1, 2-bis (pyrrol-2-yl-methyleneamino) benzene. Precursor of o-phenylenediamine (1.08g, 10mmol) was condensed with 2-pyrrolecarboxaldehyde (1.90 g, 20mmol) as described above. Yield: 1.96 g (75%). Mp: 194-196°C. ESI-MS: m/z (%): 263.2 (100) [L+H⁺]. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 6.01 (2H, s), 6.30 (2H, s), 6.40 (2H, s), 7.04 (2H, t), 7.20 (3H, t) ppm. Anal. Calcd for C₁₆H₁₄N₄: C, 73.25; H, 5.34; N, 21.41. Found: C, 73.34; H, 5.41; N, 21.26. Pale yellow rods suitable for X-ray diffraction were grown from a saturated solution of compound **a** in C₂H₅OH/CH₃CN.

Compound b of 1, 3-Bis (pyrrol-2-yl-methyleneamino) benzene. Precursor of m-phenylenediamine (1.08g, 10mmol) was condensed with 2-pyrrolecarboxaldehyde (1.90 g, 20mmol) as described above. Yield: 1.65 g (63%). Mp: 158-160°C. ESI-MS: m/z (%): 263.1(100) [L+H⁺]; ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 6.33 (2H, t), 6.71 (2H, s), 7.02 (2H, s), 7.24 (4H, s), 8.29 (2H, s) ppm. Anal. Calcd for C₁₆H₁₄N₄: C, 73.25; H, 5.34; N, 21.41. Found: C, 73.10; H, 5.41; N, 21.49. Pale yellow rods suitable for X-ray diffraction were grown from a saturated solution of compound **b** in C₂H₅OH/CH₃CN.

Compound c of 1, 4-Bis (pyrrol-2-yl-methyleneamino) benzene. Precursor of p-phenylenediamine (1.08g, 10mmol) was condensed with 2-pyrrolicarboxaldehyde (1.90 g, 20mmol) as described above. Yield: 2.10 g (80%). Mp: 213-214°C. ESI-MS: m/z (%), 263.1(100) [L+H⁺]. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 6.33 (2H, t), 6.71 (2H, s), 7.02 (2H, s), 7.24 (4H, s), 8.29 (2H, s) ppm. Anal. Calcd for C₁₆H₁₄N₄: C, 73.25; H, 5.34; N, 21.41. Found: C, 73.01; H, 5.40; N, 21.32. Pale yellow rods suitable for X-ray diffraction were grown from a saturated solution of compound **c** in C₂H₅OH/CH₃CN.

X-ray Crystallography. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation from CH₃CN/EtOH solutions. Accurate unit cell parameters were determined by a least-squares fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured on a Bruker Smart 1000 CCD or Rigaku Raxis Rapid IP diffract meter with Mo KR radiation (λ 0.71073 Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. All structures were solved by direct methods. The no hydrogen atoms were located in successive difference Fourier synthesis. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on *F*². The hydrogen atoms were added theoretically and riding on the concerned atoms. Crystallographic data and experimental details for structure analyses are summarized in Table S1. CCDC-299563-565 (for **a-c**, respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html. [Or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Fax: (+44)-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table S1. Crystal data and structure refinement for compound a-c.

Compound	c	b	a
Empirical formula	C ₁₆ H ₁₄ N ₄ (c)	C ₁₆ H ₁₄ N ₄ (b)	C ₁₆ H ₁₄ N ₄ (a)
Formula weight	262.31	262.31	262.31
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 (1)/n	Pbca	C2/c
a (Å)	10.894(2)	10.2048(10)	34.919(7)
b (Å)	9.1577(18)	15.5662(15)	17.106(3)
c (Å)	14.177(3)	17.4159(17)	14.362(3)
Alpha (deg)	90	90	90
Beta (deg)	90.888(3)	90	93.49(3)
Gamma (deg)	90	90	90
Volume (Å ³)	1414.2(5)	2766.5(5)	8563(3)
Z	4	8	24
C _{calculated} (Mg/m ³)	1.232	1.260	1.221
Absorption			
Correction (mm ⁻¹)	0.077	0.078	0.076
F (000)	552	1104	3312
Theta range (deg)	2.34-28.25	2.34-27.88	1.17-25.50
R1/wR2 [I>2sigma (I)]	0.0497/0.1404	0.0369/ 0.0914	0.1205/0.1771
R1/wR2 (alldata)	0.1153/0.1666	0.0571/0.0999	0.2855/0.2118
Largest Dif. (e.Å ⁻³)	0.141/-0.161	0.125/-0.192	0.242/-0.236

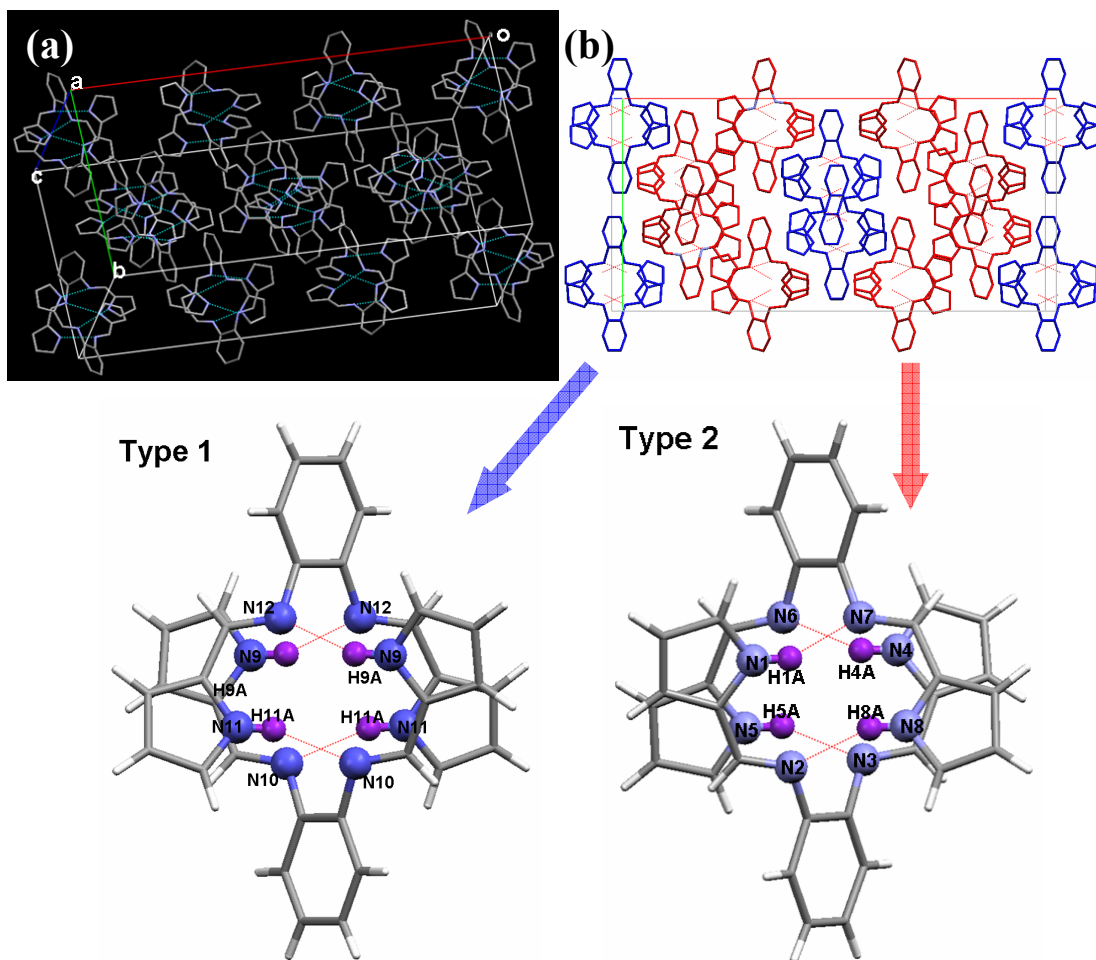


Figure S1. (a) Crystal unit cell of molecule **a**. (b) Two types of dimer are observed in one unit cell, and are blue colored for type 1 and red colored for type 2, respectively. The length and angle of hydrogen bonds in type 1 and 2 dimers are summarized in Table S2.

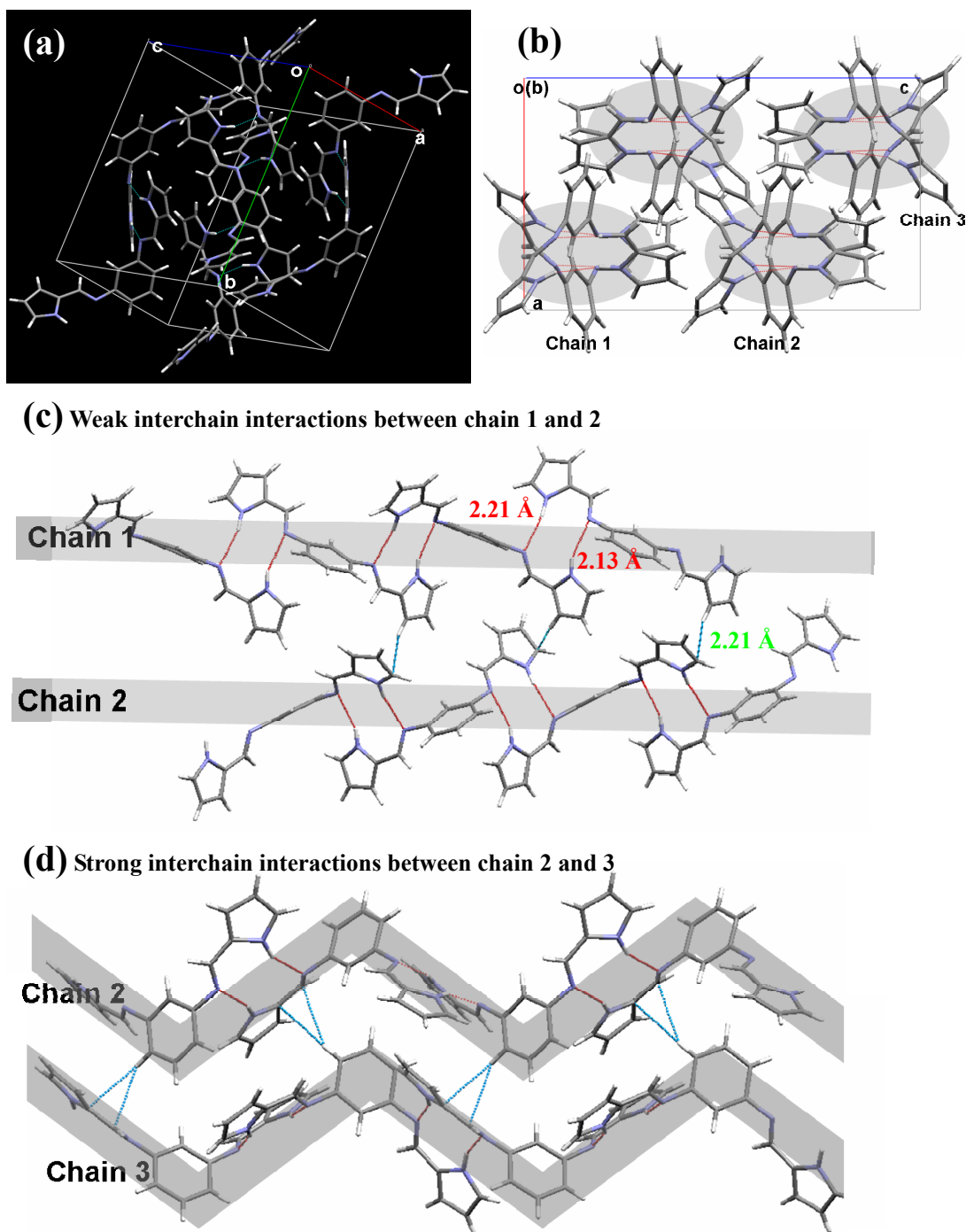


Figure S3. (a) Crystal unit cell of molecule **b**; (b) the view of the unit cell along crystal *b* axis, i.e., (010) direction, which is parallel to the hydrogen-bonded chain. (c) Side view of chain 1 and 2 labelled in (b), showing weak interchain interactions of van der Waals type. (d) Side view of chain 2 and 3 labelled in (b), showing strong interchain interactions of van der Waals type as a result of the shape match for stacking of the zigzag chains. The dash red and green lines represent the hydrogen-bonding and van der Waals contacts, respectively.

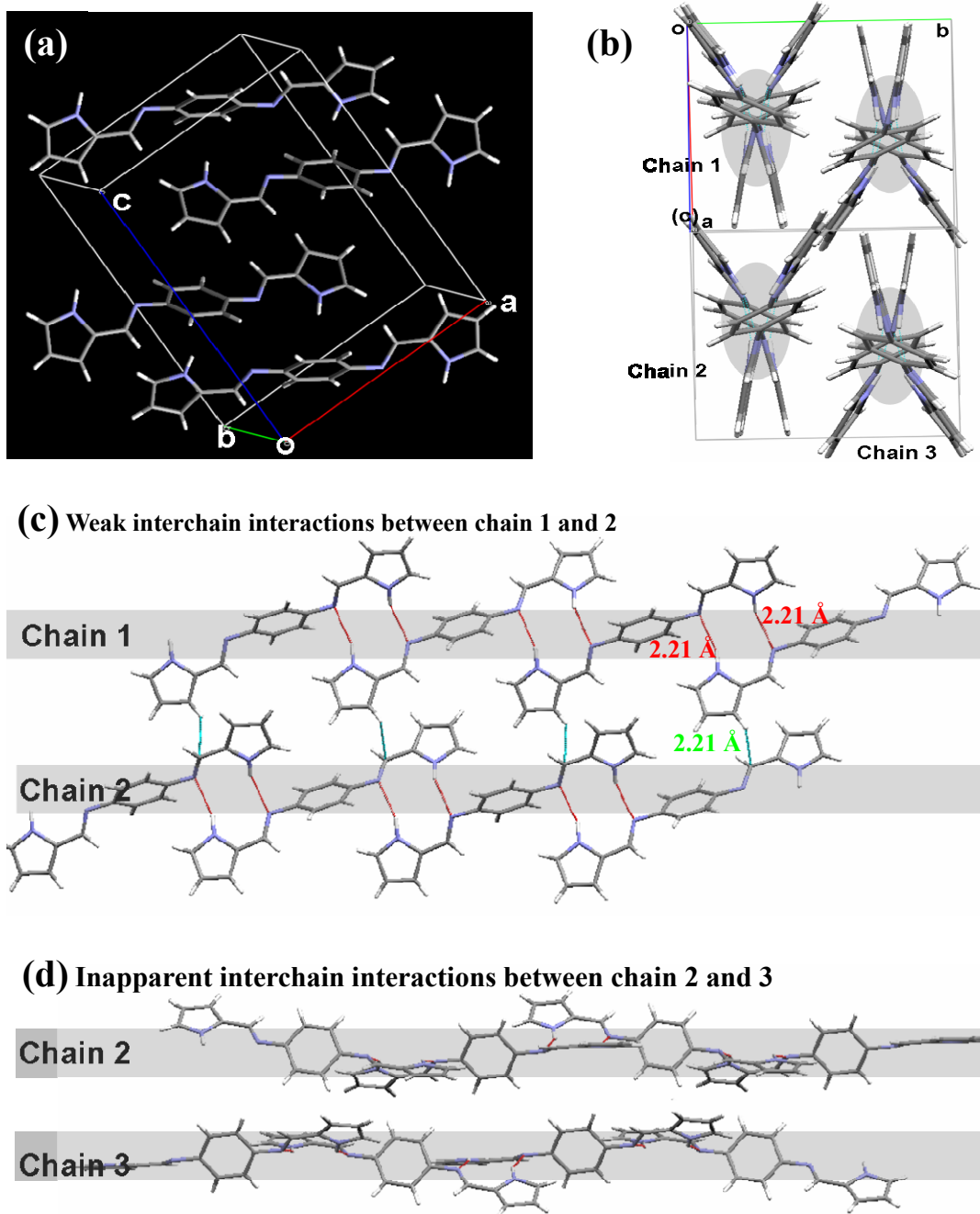


Figure S3. (a) Crystal unit cell of molecule **c**; (b) the view of the unit cell along the direction of the hydrogen-bonded chain. (c) Side view of chain 1 and 2 labelled in (b), showing weak interchain interactions of van der Waals type. (d) Side view of chain 2 and 3 labelled in (b), showing inapparent interchain interactions of van der Waals type.

Table S2. Hydrogen bonds for compound **a** based on single crystal XRD analysis.

Dimer	D-H...A	d (H...A)	∠(DHA)
Type 1	N(11)-H(11A)...N(10)#1	2.16	160.3
	N(9)-H(9A)...N(12)#1	2.13	154.9
Type 2	N(1)-H(1A)...N(7)#2	2.10	149.4
	N(4)-H(4A)...N(6)#2	2.16	154.5
	N(5)-H(5A)...N(3)#3	2.17	147.4
	N(8)-H(8A)...N(2)#3	2.16	153.5

#1 -x, y, 1/2-z

#2 1/2-x, -1/2+y, 1/2-z

#3 1/2-x, 1/2+y, 1/2-z

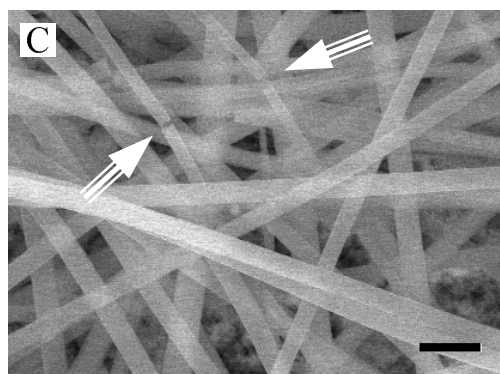
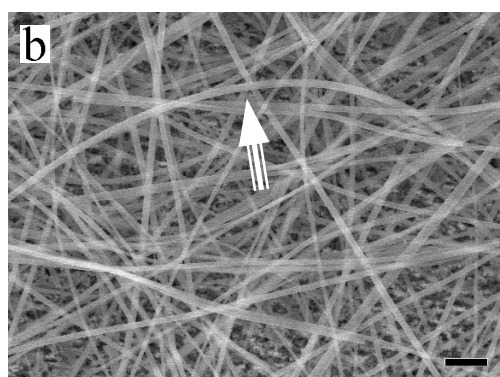
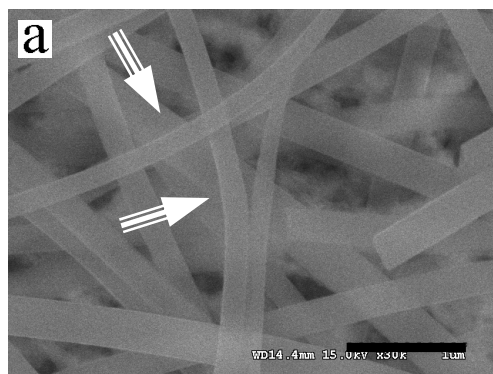


Figure S4. SEM images of the crystalline flexible nanowires of molecule **b**. (a), (b) with the moderate bend of nanostructure; (c) with the break off of the nanostructures. All the scale bars are 1 μm .

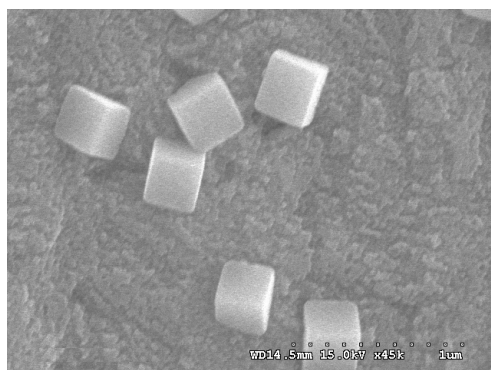


Figure S5. High-magnification SEM image of nanocubes

Full reference 1-3:

- 1 D. Horn and J. Rieger, *Angew. Chem. Int. Ed.* 2001, 40, 4331; H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda and H. Nakanishi, *Jpn. J. Appl. Phys.*, 1996, 35, L221.
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- 3 K. Balakrishnan, A. Datar, T. Naddo, J. L. Huang, R. Oitker, M. Yen, J. C. Zhao and L. Zang, *J. Am. Chem. Soc.*, 2006, 128, 7390; K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. M. Zuo and L. Zang, *J. Am. Chem. Soc.*, 2005, 127, 10496; B.-K. An, S.-K. Kwon, S.-D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, 124, 14410; F. Wang, M.-Y. Han, K. Y. Mya, Y. Wang and Y.-H. Lai, *J. Am. Chem. Soc.*, 2005, 127, 10350; F. Bertorelle, D. Lavabre and S. Fery-Forgues, *J. Am. Chem. Soc.*, 2003, 125, 6244.