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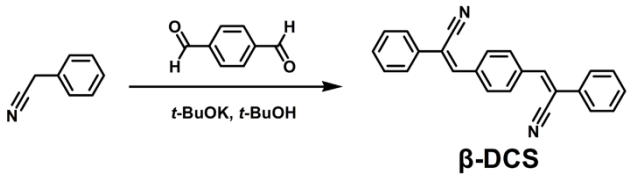
Electronic Supplementary Information

Exploring the minimal structure of wholly aromatic organogelator: simply adding two β-cyano groups into distyrylbenzene

Seong-Jun Yoon, Jong H. Kim, Jong Won Chung and Soo Young Park*

Creative Research Initiative Center for Supramolecular Optoelectronic Materials and WCU Hybrid Materials Program, Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea. E-mail: parksy@snu.ac.kr; Fax: (+82) 2-886-8331; Tel: (+82) 2-880-8327

Synthetic details for β-DCS



Scheme S1. The synthetic scheme of β-DCS

β-DCS was synthesized according to the procedure shown in Scheme S1. All chemicals were purchased commercially, and used without further purification.

(2Z,2'Z)-3,3'-(1,4-phenylene)bis(2-phenylacrylonitrile) (β-DCS) The mixture of 2-phenylacetonitrile (2.00 g, 17.07 mmol) and terephthalaldehyde (1.15 g, 8.535 mmol) in *tert*-butyl alcohol (30 mL) was stirred at 50 °C. Potassium *tert*-butoxide (1.92 g, 17.07 mmol) powder was dropped into the mixture and stirred for 2 hours. The resulting precipitate was filtered and purified by column chromatography using dichloromethane and recrystallization from dichloromethane and methanol solution. β-DCS bulk powder

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(2.40 g, 85%) was obtained after further vacuum sublimation twice. ^{1}H NMR (CDCl3) δ [ppm]: 8.00 (s, 4H, Ar-H), 7.71 (d, 4H, Ar-H), 7.56 (s, 2H, Vinyl-H) 7.45 (m, 6H, Ar-H). ^{13}C NMR (CDCl3) δ [ppm]: 140.9, 135.7, 134.5, 130.0, 129.8, 129.4, 126.4, 118.0, 113.3. m/z (EI MS) Calcd for $C_{24}H_{16}N_2$, 332.1313; Found, 332.1316. Anal. Calcd for $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43. Found: C, 86.79; H, 4.82; N, 8.41. DSB and α-DCS were synthesized according to the previously published route.[1,2]

Experimental method

Spectroscopic characterization

^{1}H NMR spectrum was recorded on a Bruker, Avance-300 (300 MHz) in $CDCl_3$ solution. ^{13}C NMR spectrum was recorded on a Bruker, Avance-500 (500 MHz) in $CDCl_3$ solution. Mass spectrum was measured using a JEOL, JMS-600W mass spectrometer. Elemental analysis was carried out using a CE instruments, EA1110 elemental analyzer. FT-IR spectrum was measured on a Thermo Scientific, Nicolet 6700 FT-IR spectrophotometer using a KBr pellet. UV-visible absorption spectra were recorded on a Shimazu, UV-1650 PC spectrometer. Photoluminescence spectra were obtained using a Varian, Cary Eclipse Fluorescence spectrophotometer. The relative fluorescence quantum yield of the β-DCS solution was measured using 9,10-diphenylanthracence (DPA) in benzene as a standard reference (1×10^{-4} mol L^{-1}, $\Phi_F = 0.83$). The absolute photoluminescence quantum efficiency of the vacuum-deposited β-DCS thin film was measured using an integrating sphere (Labsphere Co., 600 diameter). A continuous wave Xe-lamp (500 W, Melles Griot Co.) was used as the excitation light source, and a monochromator (Acton Research Co.) attached to a photomultiplier tube (Hamamatsu) was used as the optical detector system. All of the systems were calibrated using a tungsten-halogen standard lamp and deuterium lamp (Ocean Optics LS-1-CAL and DH-2000-CAL, respectively). Φ_{PL} was calculated based on the de Mello method.[3] Time-resolved fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique with a FluoTime200 spectrometer (PicoQuant) equipped with a

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PicoHarp300 TCSPC board (PicoQuant) and a PMA182 photomultiplier (PicoQuant). The excitation source was a 377 nm picoseconds pulsed diode laser (PicoQuant, LDH375) driven by a PDL800-D driver (PicoQuant) with fwhm ~70 ps. The decay time fitting procedure was carried out with the IRF by using a Fluofit software (PicoQuant). The smallest residual value was controlled during the fitting and simulation ($\chi^2 = 1.035$).

X-ray and morphological analysis

XRD measurements were performed on a Bruker, powder X-ray diffractometry, operating at 3 kW (Cu Kα, $\lambda = 1.5418$ Å). FE-SEM images were acquired on a Carl Zeiss, SUPRA 55VP.

Quantum chemical calculation

Single molecule calculations were performed at the density functional theory (DFT) level of theory with the Gaussian09 software.[4] Herein, the ground state geometry in the gas phase was fully optimized using the B3LYP functional and 6-31G** basis set.

Device fabrication and measurement

Before device fabrication, SiO_2/Si (300 nm-thick SiO_2) substrates were rinsed by sonication in acetone and *iso*-propyl alcohol. Then the substrates were exposed to UV (360 nm) for 10 min. For the device of β-DCS supramolecules, we grew crystalline β-DCS supramolecules by keeping vertical substrates inside the vial containing 0.05 wt% β-DCS solution in dichloromethane. After slow evaporation of solvent for two days, β-DCS supramolecules were grown onto SiO_2/Si substrates. After completing solvent evaporation, the residual solvent was further eliminated by vacuum for several hours. These substrates were carried into a N_2-filled glovebox and top-contact gold electrodes (50 nm-thick) were thermally deposited under a vacuum of 3×10^{-6} Torr at a deposition rate of 0.3~0.4 Å s^{-1}. For the device of vacuum-deposited β-DCS thin film, the cleaned and UV-treated substrates were carried into a N_2-filled glovebox and the active layer (β-DCS) was deposited (50 nm-thick) by thermal evaporation under a vacuum of 7×10^{-7} Torr at a deposition rate of 0.1~0.2 Å s^{-1}. Finally top-contact gold electrodes (50 nm-thick) were thermally

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deposited under the same condition as that of the device of β-DCS supramolecules. The channel length (L) and width (W) defined by a shadow mask were 50 μm and 1 mm. All electrical characteristics of devices were measured using a Keithley 4200 semiconductor parameter analyzer connected to a probe station in a nitrogen-filled glovebox.

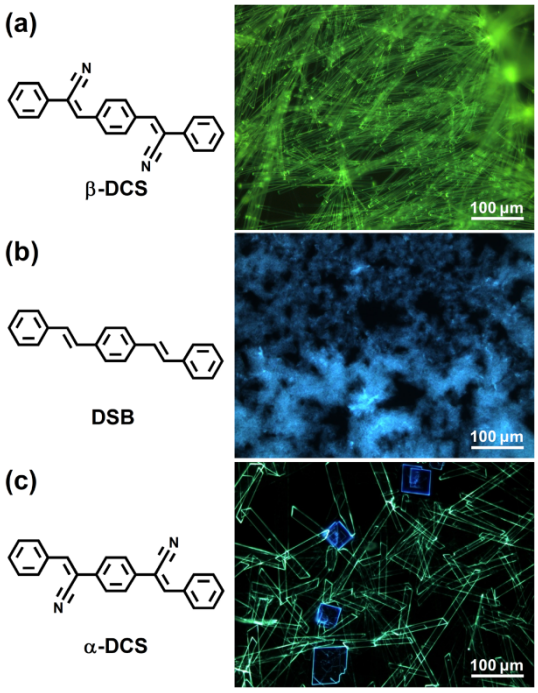

Fig. S1 Molecular structures and fluorescence microscopy images of corresponding self-assembled architectures obtained via drop-casting: (a) β-DCS (1D wire structure). (b) DSB (unstructured agglomerate). (c) α-DCS (2D crystal structure).

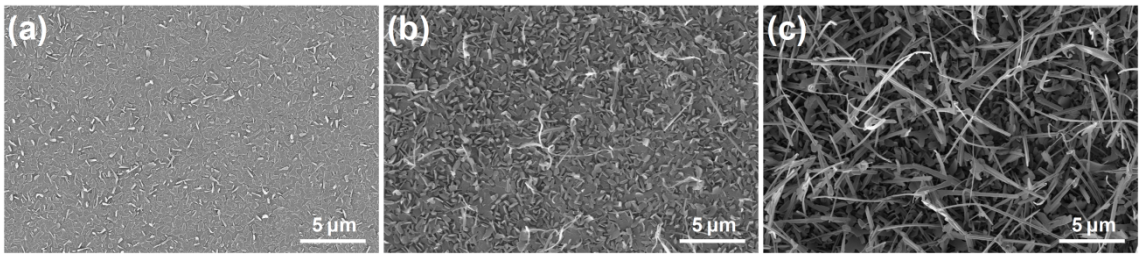

Fig. S2 SEM images of vacuum-deposited β-DCS film on glass substrate for various film thicknesses: (a) 50 nm, (b) 100 nm, (c) 500 nm.

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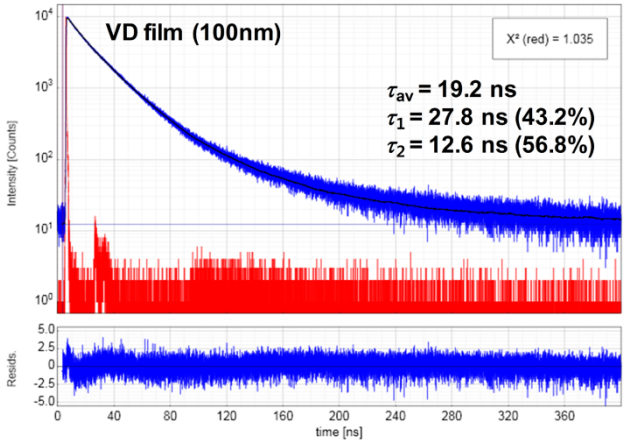

Fig. S3 Fluorescence decay profiles of the vacuum-deposited β-DCS thin film (blue line) and IRF (red line). Black line shows the fitting curve and lower line shows the residual.

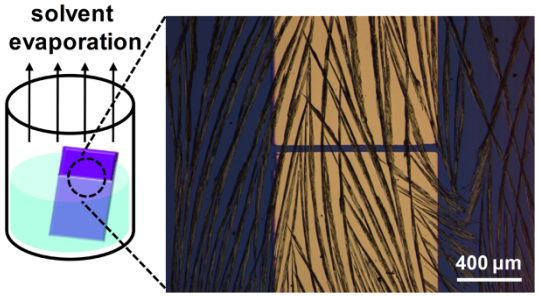

Fig. S4 Schematic illustration of the solvent evaporation method for the growth of oriented supramolecules on a vertical substrate from an organic solution and optical image of a typical device fabricated from β-DCS.

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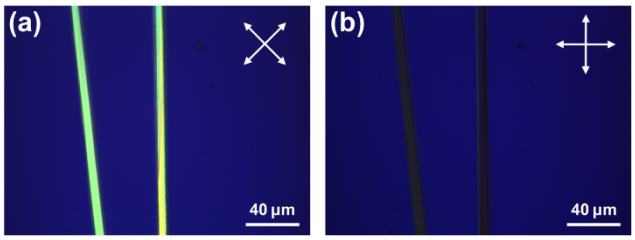

Fig. S5 Polarized optical microscopy images of 1D β-DCS supramolecules with the different cross polarization directions ((a) and (b)).

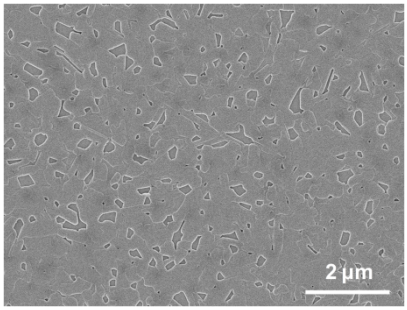

Fig. S6 SEM image of vacuum-deposited β-DCS film (thickness of 50 nm) on SiO_2/Si substrate.

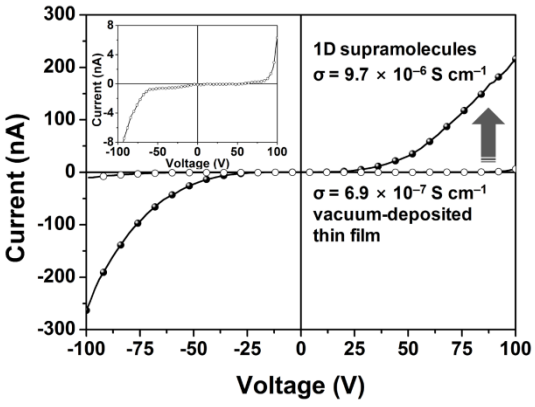

Fig. S7 Typical *I–V* curves of β-DCS supramolecules (filled symbols) and vacuum-deposited thin film (thickness = 50 nm, open symbols). Inset shows the enlarged *I–V* curve of vacuum-deposited β-DCS thin film.

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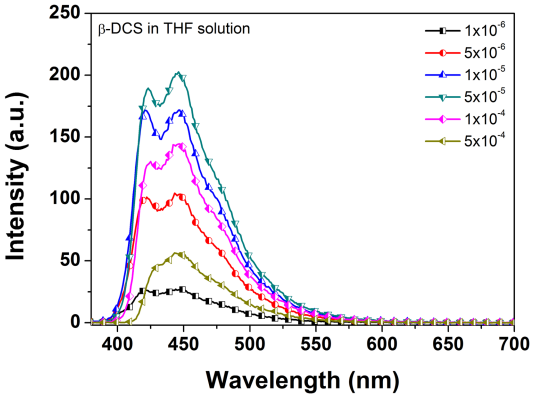

Fig. S8 Photoluminescence spectra of β-DCS in THF solution depending on the concentration.

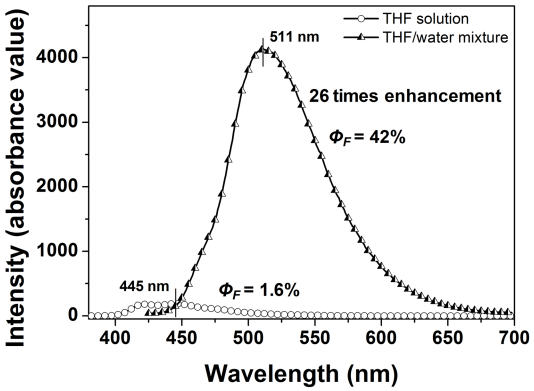

Fig. S9 Photoluminescence spectra of β-DCS in THF solution ($c = 2 \times 10^{-5}$ mol L^{-1}, open symbols) and THF/water mixture ($c = 2 \times 10^{-5}$ mol L^{-1}, half filled symbols).

References

1 C. C. Wu, M. C. DeLong, Z. V. Vardeny and J. P. Ferraris, *Synth. Met.*, 2003, **137**, 939.

2 S. J. Yoon and S. Y. Park, *J. Mater. Chem.*, 2011, **21**, 8338.

3 J. C. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.*, 1997, **9**, 230.

4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani,

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V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.