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Supporting Information for

A Distyrylbenzene Based Highly Efficient Near-Infrared Emitting Organic Solid

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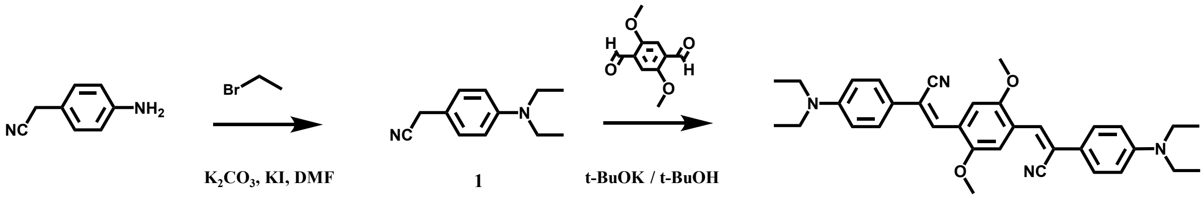
General Methods

Commercially available chemicals were used as received. All glasswares and magnetic stirring bars were thoroughly dried in an oven (60 °C). Reactions were monitored using thin layer chromatography (TLC). Commercial TLC plates (silica gel 254, Merck Co.) were developed and the spots were visualized under UV light at 254 or 365 nm. Silica gel column chromatography was performed with silica gel 60 G (particle size 5–40 µm, Merck Co.). ^{1}H and ^{13}C NMR spectra were collected with a Bruker AVANCE-300 NMR spectrometer. Chemical shifts (δ) are given in ppm and referenced to TMS. Mass spectra were measured using a JEOL, JMS-600W mass spectrometer. Elemental analyses were carried out using a CE instruments, EA1110 elemental analyzer.

Synthesis



***β*-MODEADCS**

Scheme S1. Synthesis of (2Z,2'Z)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(2-(4-(diethylamino)phenyl)acrylonitrile) (β-MODEADCS).

2-(4-(Diethylamino)phenyl)acetonitrile (1)

To a solution of 2-(4-Aminophenyl)acetonitrile (2 g, 15.1 mmol) in dry DMF (20ml), were added K_2CO_3 (4.6 g, 33.2 mmol) and KI (catalytic amount) and the mixture was stirred at 80 °C. Bromoethane (2.5ml, 33.3 mmol) was slowly dropped into the mixture. The reaction lasted overmight. After cooling to room temperature, the mixture was poured into brine and extracted with dichloromethane. The organic phase dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product (2.44 g, 86 %) was obtained by column chromatography using ethyl acetate and n-hexane (1:6 v/v). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 7.13(d.2H), 6.63(d.2H), 3.60 (d.2H), 3.35(q.4H), 1.14(t.6H).

(2Z,2'Z)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(2-(4-(diethylamino)phenyl)acrylonitrile) (β-MODEADCS) (β-MODEADCS)

The mixture of 2-(4-(diethylamino)phenyl)acetonitrile (1.24 g, 6.6 mmol) and 2,5-dimethoxyterephthalaldehyde (0.64 g, 3.3 mmol) in tert-butyl alcohol (15 ml) was stirred at 50 °C. Potassium tert-butoxide (0.74 g, 6.6 mmol) powder was dropped into the mixture and stirred for 2 hours. After that, it was quenched with methanol. The resulting precipitate was filtered and purified by column chromatography using dichloromethane and recrystallization from dichloromethane and methanol solution. Red powder of β-MODEADCS (2.3 g, 65 %) was obtained after recrystallization three times in ethanol. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 7.87(s.2H), 7.79(s.2H), 7.56(d.4H), 6.70(d. 4H), 3.95(s.6H), 3.42(q), 1.21(t.12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm]: 151.8, 148.5, 130.6, 127.5, 125.6,121.7, 119.1, 111.7, 110.1, 56.5, 44.6, 12.7. HRMS (ESI+, m/z): $[M]^+$ calcd for $C_{34}H_{38}N_4O_2$, 534.2995; found, 534.2999. Anal. calcd for $C_{34}H_{38}N_4O_2$: C 76.37, H 7.16, N 10.48, O 5.98; found: C 76.27, H 7.13, N 10.33, O 6.17.

Spectroscopic characterization

UV-visible absorption spectra were recorded on a Cary 5000 absorption spectrometer (Varian). Solid-state UV-visible absorption spectra were recorded with reflectance mode. Photoluminescence spectra were obtained using a Varian, Cary Eclipse Fluorescence spectrophotometer. Emission spectra were corrected for the sensitivity of the detection unit. The absolute photoluminescence quantum efficiencies of the single crystal, powder, solution, and nanoparticle samples were measured using a C9920 absolute PL quantum yield measurement system (Hamamatsu) equipped with an integrating sphere. A 10 mm path length quartz cuvette for solution and nanoparticle suspension samples was set in the integrating sphere using an appropriate cuvette holder. Time-resolved fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique with a FluoTime200 spectrometer (PicoQuant) equipped with a PicoHarp300 TCSPC board and a PMA182 photomultiplier. The excitation source was a 377 nm picosecond pulsed diode laser driven by a PDL800-D driver with FWHM ~70 ps. The decay time fitting procedure was carried out with the IRF by using the Fluofit software. The smallest residual value was asserted during the fitting and simulation. For the single crystal measurements, small crystals were selected (typical size ~ 700 μm for minimum axis length) and the crystals were adjusted in such a way in the spectrometers that reabsorption was minimized.

Computational details

Ground state (S_0) and first singlet excited state (S_1) geometry of β-MODEADCS was computed using the B3LYP level of density functional theory (DFT),[1] in which the 6-311G* basis set was applied for all atoms. Vertical transition energies of the molecule was calculated at the time-dependent (TD-)DFT. S_0 geometry from single crystal X-ray analysis data was adopted to compute the vertical transition energy for the β-MODEADCS dimer. CAM-B3LYP level of theory, with 6-311g** basis set was applied for the dimer calculation. All calculations were carried out using Gaussian 09.[2]

X-ray analysis

Single crystal structures were analyzed by using SMART–APEX II ULTRA (Bruker) in Central Instrument Facility, Gyeungsang National University.

The power XRD patterns were recorded using a sealed-tube generator (900 W) equipped with a pinhole Cu-Kα (λ = 1.542 Å) parallel beamline based on a home-mounted Kirkpatrick-Baez optics coupled with a HiStar detector (Bruker AXS).

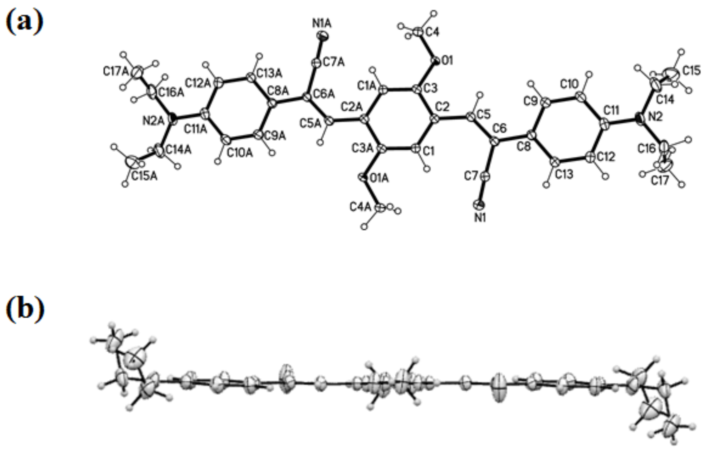


Figure S1. ORTEP drawing of β-MODEADCS single crystal. (a) top view, (b) side view.

Table S1. Crystal data and structure refinement for β-MODEADCS.

Identification code	b-MODEADCS	
Empirical formula	C34 H38 N4 O2	
Formula weight	534.68	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 4.7039(2) Å	α= 100.068(2)°.
	b = 9.3029(3) Å	β= 92.587(2)°.
	c = 16.8491(6) Å	γ = 99.396(2)°.
Volume	714.16(5) Å^3	
Z	1	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	286	
Crystal size	0.33 x 0.27 x 0.10 mm^3	
Theta range for data collection	1.23 to 28.45°.	
Index ranges	-6<=h<=6, -12<=k<=12, -22<=l<=22	
Reflections collected	19580	
Independent reflections	3574 [R(int) = 0.0305]	
Completeness to theta = 28.45°	99.2 %	
Absorption correction	Multi-scan SADABS	
Max. and min. transmission	0.9921 and 0.9749	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3574 / 0 / 181	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1601	
R indices (all data)	R1 = 0.0656, wR2 = 0.1712	
Largest diff. peak and hole	0.302 and -0.271 e.Å^{-3}	

Fluorescence of β-MODEADCS Nanoparticles

Nanoparticle sample was prepared by precipitating β-MODEADCS in THF:water mixture (1:99 v/v). The PL quantum yield of nanoparticle ($\Phi_F = 0.06$) is drastically reduced against solution due to strongly reduced radiative rates by H-type exciton coupling as well as by an enhanced non-radiative rate attributed to high trap concentrations in the polycrystalline nanoparticle suspensions

Fluorescence Decay Kinetics

Solution

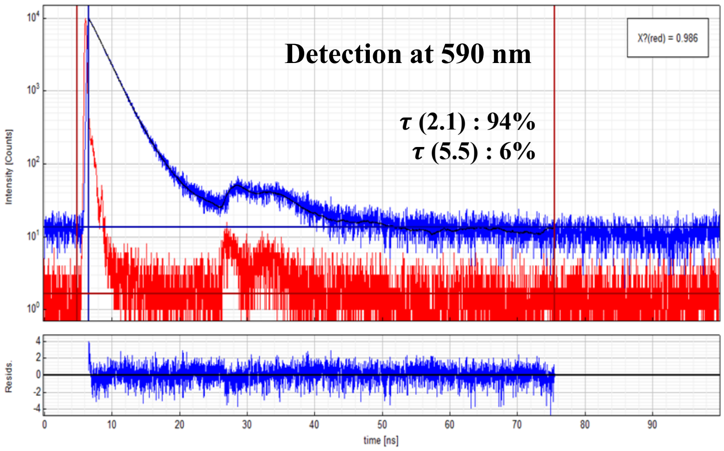


Figure S2. Fluorescence decay profiles of the β-MODEADCS solution (blue line) collected at 590nm and IRF (red line). Black line shows the fitting curve and lower line shows the residual.

Pristine powder

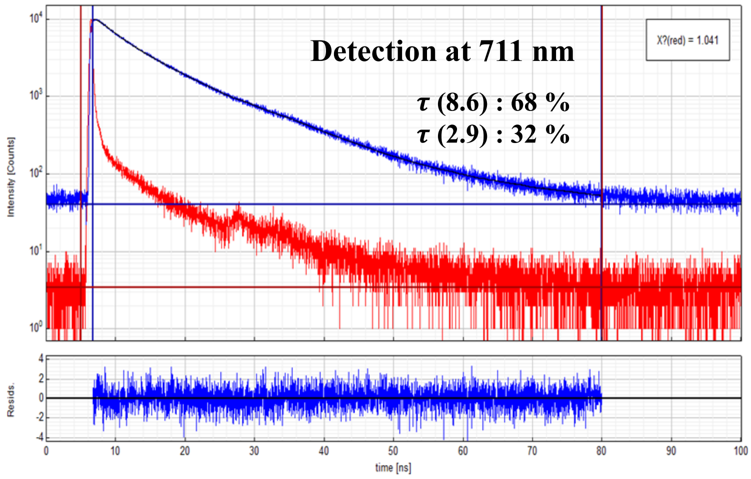


Figure S3. Fluorescence decay profiles of the β-MODEADCS powder (blue line) collected at 711 nm and IRF (red line). Black line shows the fitting curve and lower line shows the residual.

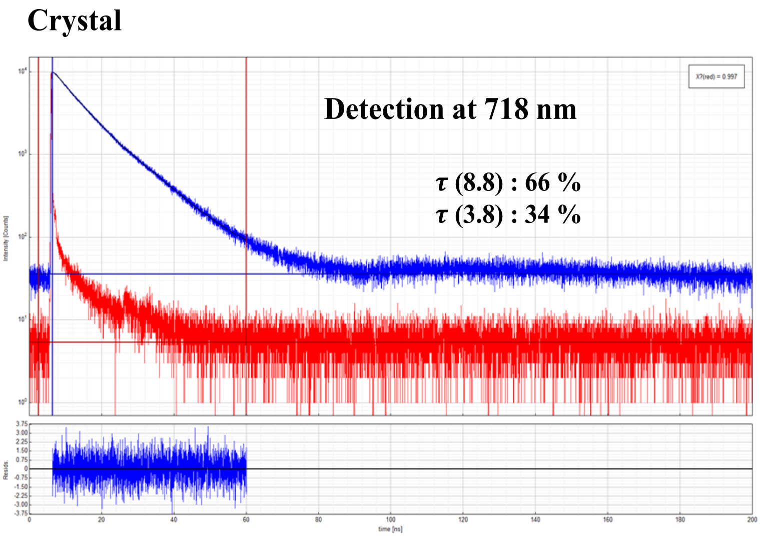


Figure S4. Fluorescence decay profiles of the β-MODEADCS crystal (blue line) collected at 718 nm and IRF (red line). Black line shows the fitting curve and lower line shows the residual.

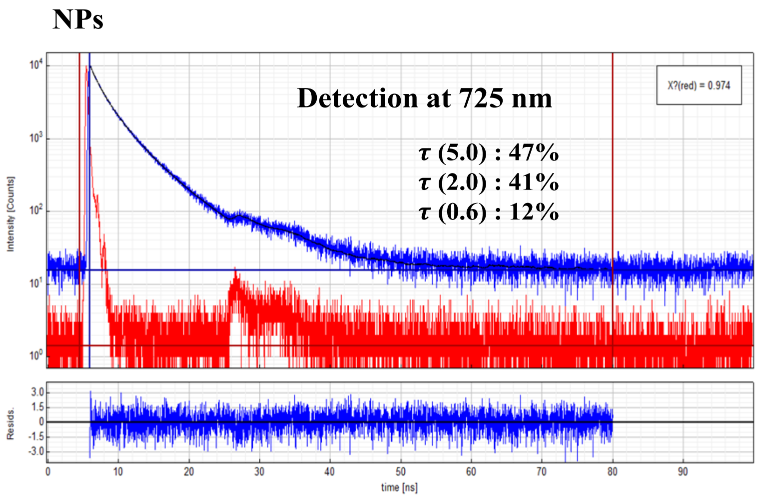


Figure S5. Fluorescence decay profiles of the β-MODEADCS nanoparticles (blue line) collected at 725nm and IRF (red line). Black line shows the fitting curve and lower line shows the residual.

The lifetime of β-MODEADCS in solution is slightly non-exponentially which reflect the presence of excited state planarization, as discussed earlier for this class of compounds.[3] In single crystals and pristine powder samples, (unavoidable) reabsorption gives rise to non-exponential lifetimes. For the nanoparticle sample, non-exponential lifetimes reflect mainly the presence of trap states.

Computational Results

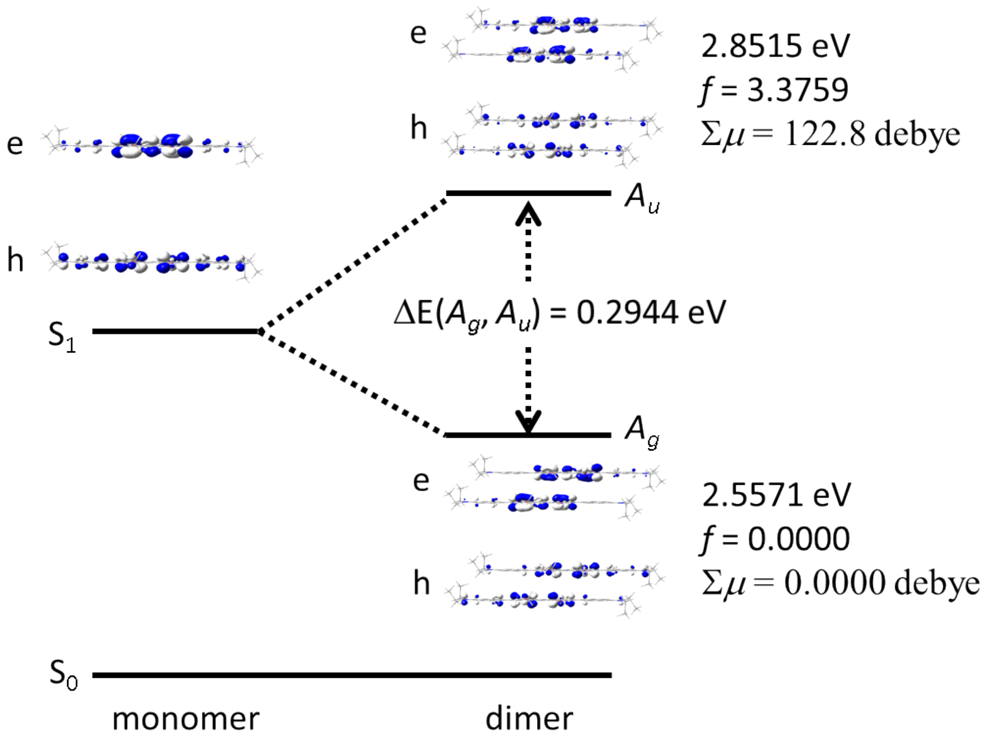


Figure S6. TD-DFT results for β-MODEADCS. Natural transition orbital (NTO) analysis for monomer and dimer species.

Powder XRD

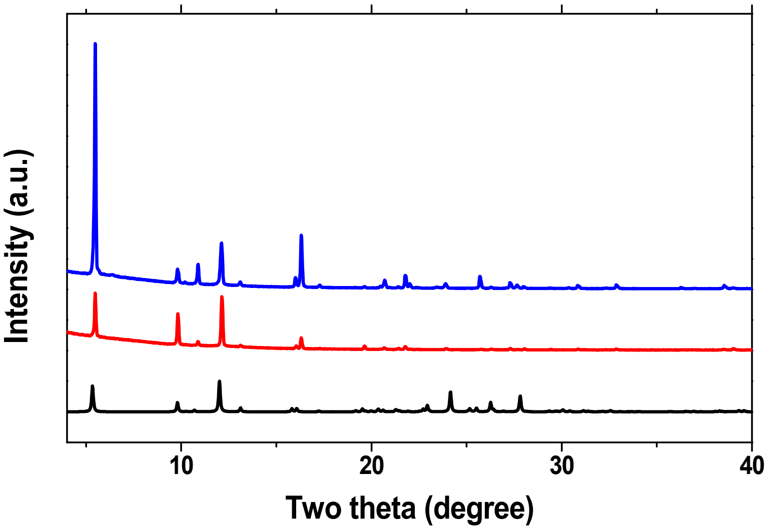


Figure S7. Powder XRD patterns of β-MODEADCS: simulated powder XRD pattern of the single crystal (black line), powder (red line), and single crystal (blue line).

References:

1. (a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, 37, 785. (b) A. D. Becke, *J. Chem. Phys.* 1993, 98, 5648.

2. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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