Supporting Information for

Novel Photochromic Infinite Coordination Polymer Particles Derived from Diarylethene Photoswitch

Xiao Guang Hu,[a] Xiao Liang Li,[b]* Sung Ik Yang[a]*

[a] Department of Applied Chemistry, Kyung Hee University, Yongin-Si 446-701, Republic of Korea.

[b] Department of Chemistry, Hebei University of Engineering, Handan 056038, P.R.China.

*Corresponding Author. E-mail: siyang@khu.ac.kr; xiaoliangli@khu.ac.kr

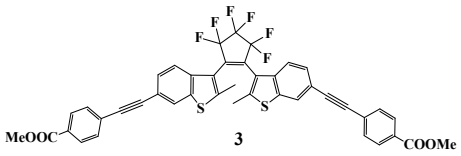
Table of Contents

1. Methods and Materials

All reagents and spectrograde solvents were purchased from Sigma-Aldrich, TCI and SAMCHUN and used as received. The ^{1}HNMR and ^{13}C NMR spectra were obtained using a JEOL JNM-AL300 spectrometer at 300 in $CDCl_3$, DMSO-d6, with tetramethylsilane as the internal reference. High resolution mass spectrometry (HRMS) spectra were obtained with JEOL JMS-700 spectrometer. Fourier transform infrared (FT-IR) spectroscopy measurements were performed using a JASCO FTIR-4200 instrument. TGA was performed using a TGA Q5000 IR / SDT Q600 (TA) Thermal Analyzer. FE-TEM was performed using a JEM-2100F (JEOL) Field Emission Transmission Electron Microscopy. FE-SEM was performed using a LEO SUPRA 55, GENESIS 2000 (Carl Zeiss, EDAX) Field Emission Scanning Electron Microscope. BET was performed using a BELSORP-max (MP) BET Surface area and Pore size Analyzer. Flash column chromatography was performed with Merck silica gel 60 (70-230 mesh). UV and visible irradiations were performed with standard lamps used for visualizing TLC plates (VL6L; 312 nm, 8 mW/cm^{-2}) and a 400 W tungsten lamp and the samples were placed in a glass chamber maintained at room temperature. UV absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in spectroscopy grade DMF. Photochromic changes were monitored using a 500 W xenon lamp (Newport-74000) equipped with a monochromator (Newport- 66921).

2. Experimental Procedures

Compound 3

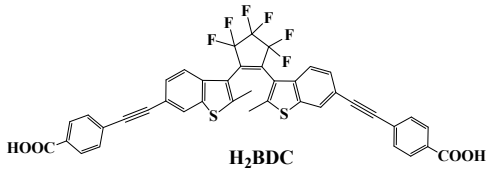


3

To a 100mL two-neck flask was loaded **1**[1] (920 mg, 1.28 mmol), **2**[2] (491mg, 3.07 mol), CuI (28 mg, 0.15 mmol) and $Pd(PPh_3)_2Cl_2$ (50 mg, 0.07 mmol). Then degased triethyl -amine (40 mL) was added. The reaction mixture was heated to reflux overnight. The resulting mixture was cooled to room temperature, solvent was evaporated under a reduced pressure. Then the residue was purified by column chromatography (SiO_2, EA:Hexane = 10:1) to afford brown yellow solid (552 mg, 0.71 mmol) of **3** in a 54.95% yield.

^{1}**HNMR** (300 MHz, $CDCl_3$): δ (ppm): 2.23 (s, 3.6H), 2.49 (s, 2.4H), 3.92 (s, 6H), 7.34-8.03 (m, 14H). ^{13}**CNMR** (300 MHz, $CDCl_3$): δ (ppm): 166.4, 147.7, 138.2, 138.1, 132.4, 131.5, 131.4, 129.5, 128.1, 128.0, 127.7, 125.5, 125.3, 121.9, 121.7, 119.1, 118.9, 92.0, 89.3, 52.3, 52.2, 15.3. **HRMS** (FAB+): *m/z* calcd. for $C_{43}H_{26}F_6O_4S_2$ 784.1177, found [M+H] 785.1265

H_2BDC[3]



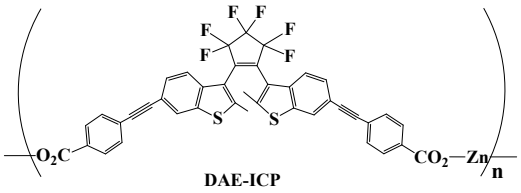
H_2BDC

To a stirred solution (30 mL, $EtOH/H_2O/CH_2Cl_2$ = 9:1:5, V/V) of **3** (671 mg, 0.86 mmol) was added KOH (480 mg, 8.6 mmol) at room temperature. Then the reaction

mixture was heated to 35°C for 12h，monitored by TLC plate. The resulting mixture was cooled to room temperature, then the mixture was filtered over a Buchber funnel and the collected solid was washed with CH_2Cl_2 and deionized water. The solid product was then dried at 60°C for 12 h. Finally, got light yellow solid (645 mg, 0.85 mmol) of **H_2BDC** in a 99.11% yield.

^{1}HNMR (300 MHz, DMSO-d6): δ (ppm): 2.32 (s, 3.0H), 2.53(s, 23.0H), 7.40-8.22 (m, 14H), 13.17 (s, 2H). **^{13}CNMR** (300 MHz, DMSO-d6): δ (ppm):166.7, 145.8, 137.8, 137.7, 131.5, 131.4, 130.7, 130.6, 129.6, 129.5, 128.3, 128.0, 126.4, 126.0, 125.7, 121.8, 118.0, 117.9, 91.7, 91.6, 89.2, 15.0. **HRMS** (FAB+): *m/z* calcd. for $C_{41}H_{22}F_6O_4S_2$ 756.0864, found [M] 756.0872.

DAE-ICP[4-7]

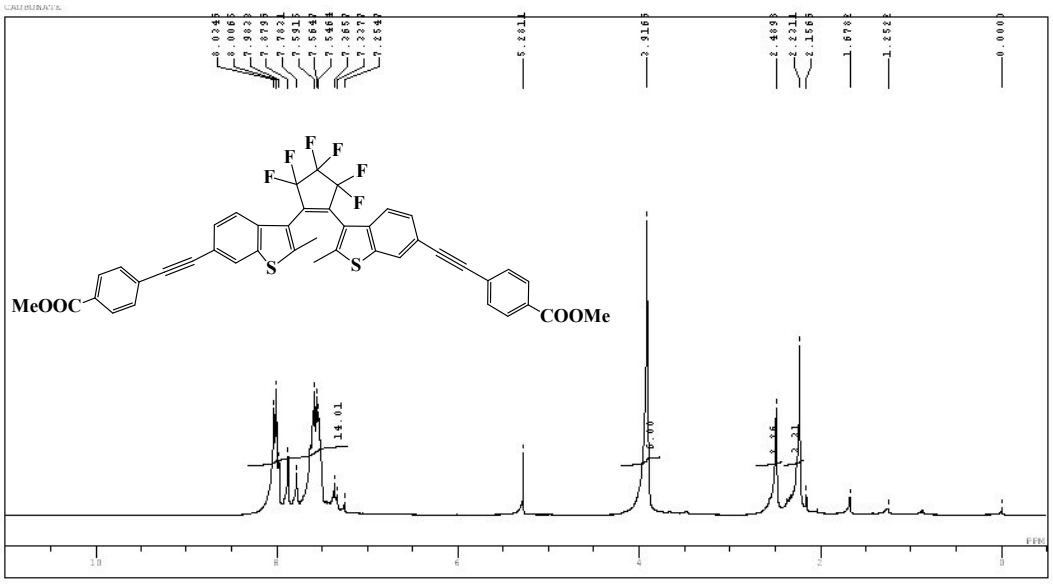


DAE-ICP

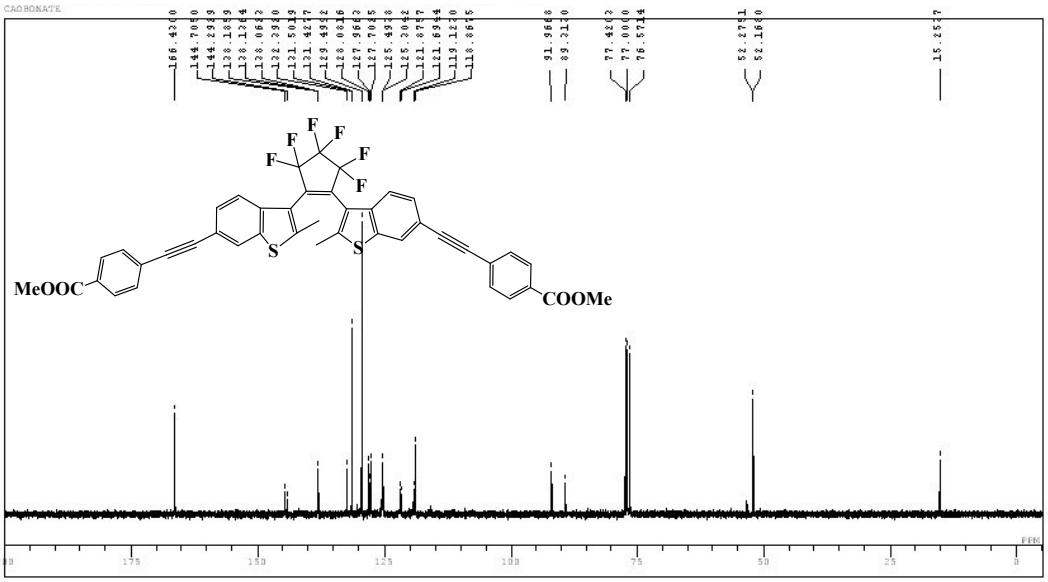
H_2BDC (56.6 mg, 0.075 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (65.0 mg, 0.219 mmol) was dissolved in 7.4 mL of DMF in a 20mL screw top vial, the solution was dispensed evenly into 10 vials(5mL size), then the vials were kept standing at 100°C in an oven for 24h.The samples were cooled to room temperature slowly, collected with a nylon membrane filters (0.45μm, diameter 47 mm) and washed with fresh DMF, then $CHCl_3$. The solid product was then dried in oven at 200°C for 12 h to release DMF. Finally, yellow solid (17.5mg) of **DAE-ICP** was afforded.

3. NMR spectra

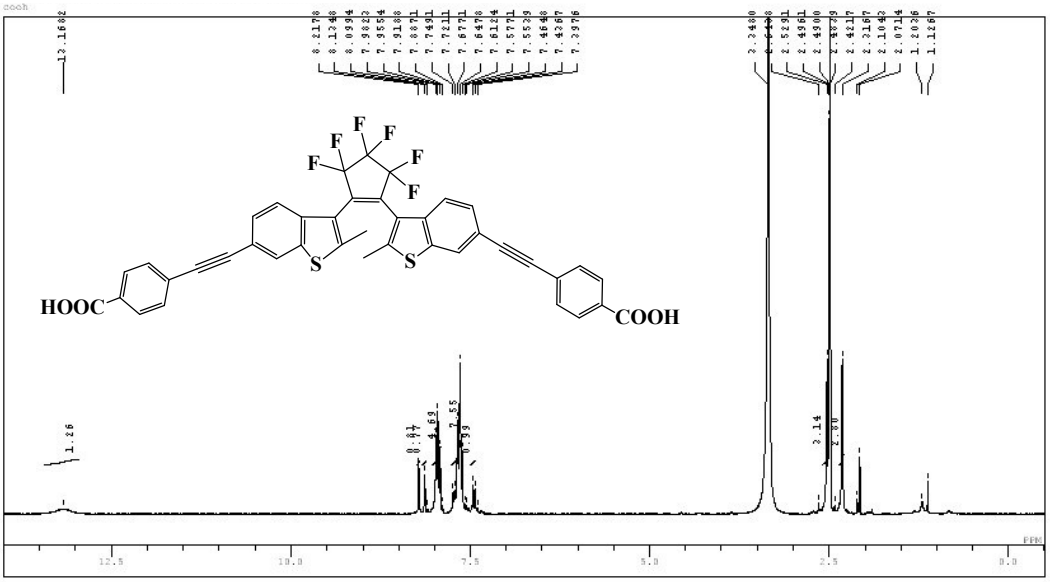
[1]HNMR of compound 3



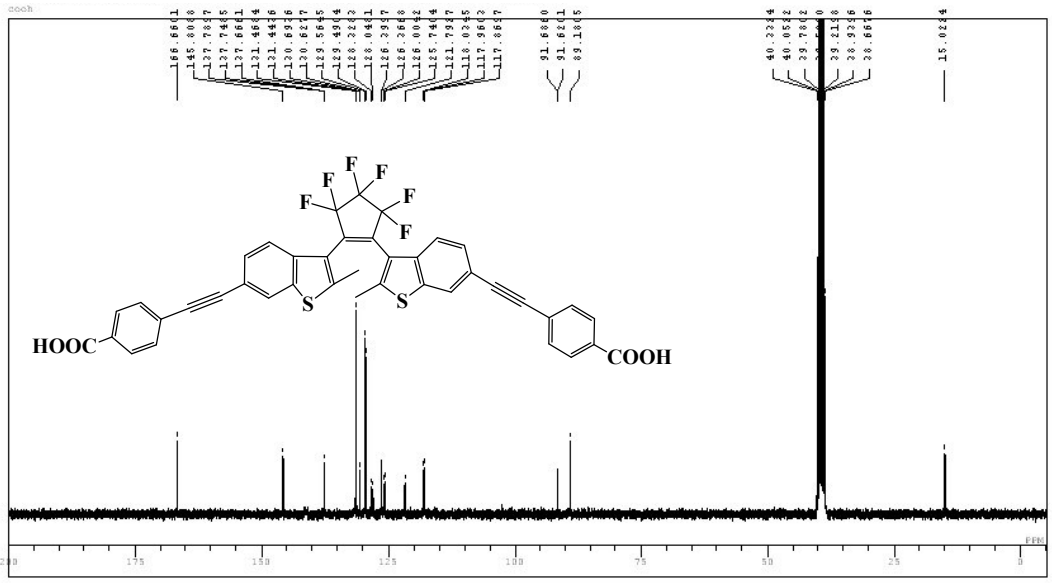
[13]CNMR of compound 3



^{1}HNMR of H_2BDC



^{13}CNMR of H_2BDC



4. EDX spectra of DAE-ICP

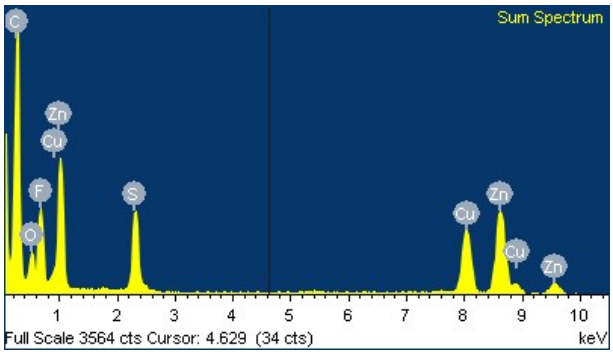


Fig. S1 EDX spectra of **DAE-ICP**.

5. Photo-graphic images of solid state H_2BDC

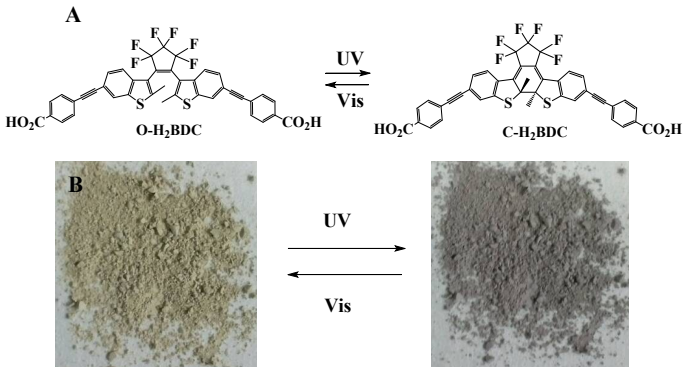


Fig. S2 (A) The conformational change of ligand **H_2BDC** upon irradiation with UV and visible light; (B) Photo-graphic images of solid state **H_2BDC** upon alternative irradiation with UV and Visible light.

6. FT-IR spectra

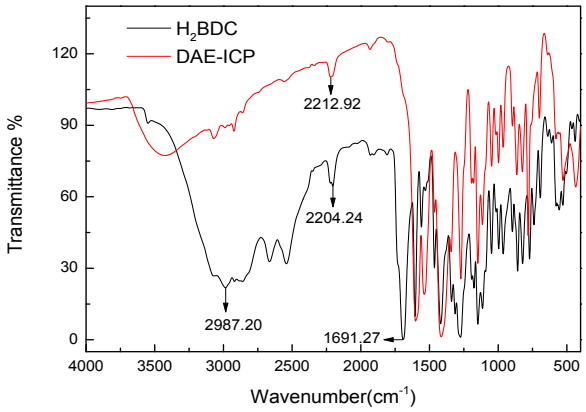


Fig. S3 FT-IR spectra of **H_2BDC** and **DAE-ICP**.

7. Nitrogen adsorption isotherm of DAE-ICP

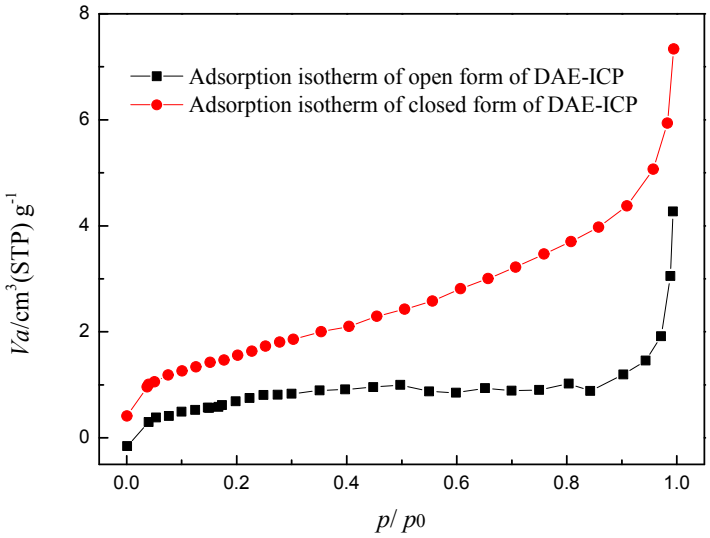


Fig. S4 Nitrogen adsorption isotherm of **DAE-ICP** measured at 77 K: (black squre- open form; red circle- close form).

8. Brunauer–Emmett–Teller (BET) of DAE-ICP

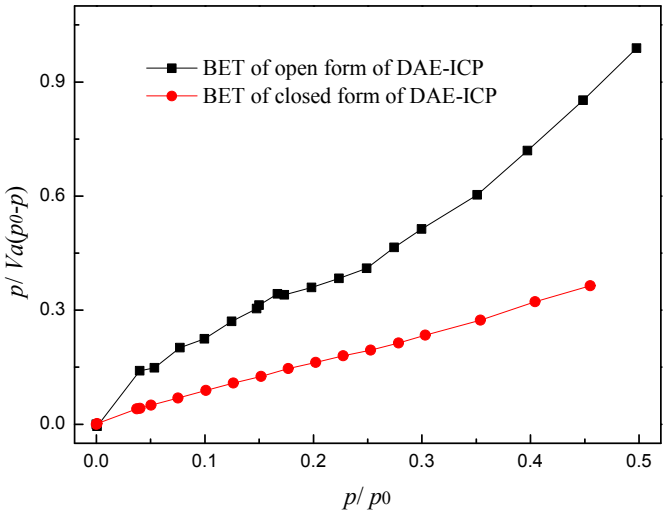


Fig. S5 Brunauer–Emmett–Teller (BET) of **DAE-ICP** measured in N_2 at 77 K.

9. TGA diagram of activated DAE-ICP

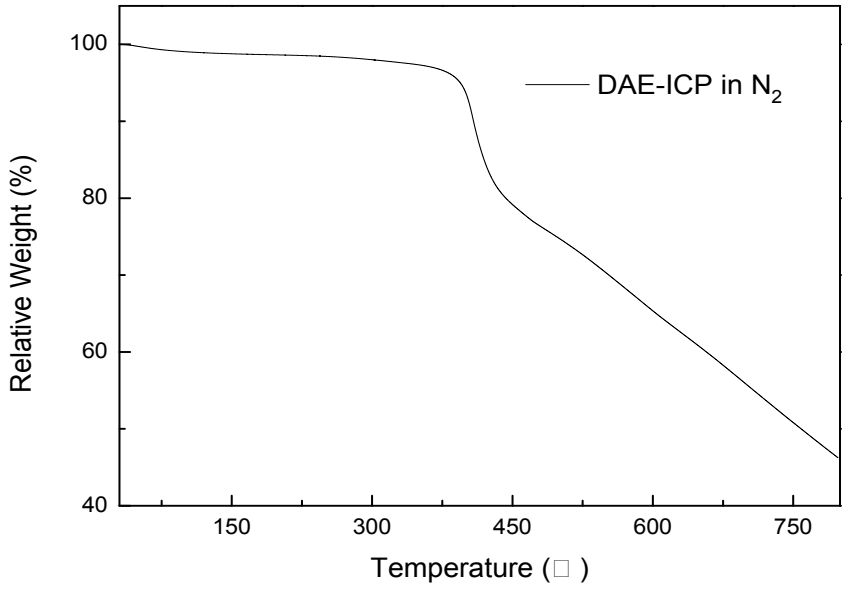


Fig. S6 TGA diagram of **DAE-ICP**.

10. Reference

1. K. Matsuda and M. Irie, *Chemistry – A European Journal*, 2001, **7**, 3466-3473.
2. A. C. Pauly and P. Theato, *Journal of Polymer Science Part A: Polymer Chemistry*, 2011, **49**, 211-224.
3. C. Mizuno, A. Chittiboyina, A. Patny, T. Kurtz, H. Pershadsingh, R. Speth, V. Karamyan and M. Avery, *Medicinal Chemistry Research*, 2009, **18**, 611-628.
4. T. Gadzikwa, B.-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chemical communications*, 2008, 3672-3674.
5. H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science*, 2010, **327**, 846-850.
6. A. R. Millward and O. M. Yaghi, *Journal of the American Chemical Society*, 2005, **127**, 17998-17999.
7. T. Ishiwata, Y. Furukawa, K. Sugikawa, K. Kokado and K. Sada, *Journal of the American Chemical Society*, 2013, **135**, 5427-5432.