ADVANCED MATERIALS

Supporting Information

for

Advanced Materials, adma.200702210

Supporting Information for *Adv. Mater.* adma.200702210

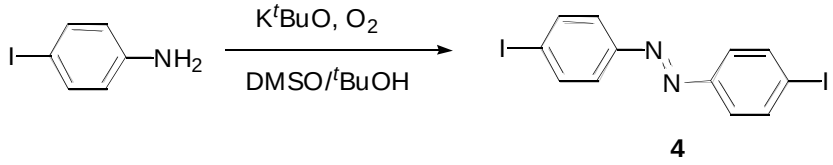
Polymerizable Photochromic Macrocyclic Metallomesogens: Design of Supramolecular Polymers with Responsive Nanopores **

Cory S. Pecinovsky, Evan. S. Hatakeyama, and Douglas L. Gin*

Materials and General Procedures. All syntheses were carried out under a dry argon atmosphere with using Schlenk line techniques. All solvents and reagents were purchased from the Aldrich Chemical Co., unless otherwise noted. Triethylamine was distilled over sodium under argon and used as required. Dichloromethane was distilled over CaH_2, and used as required. 5-Bromo-pyridin-3-ol was obtained from Adesis (catalog # 2-265).

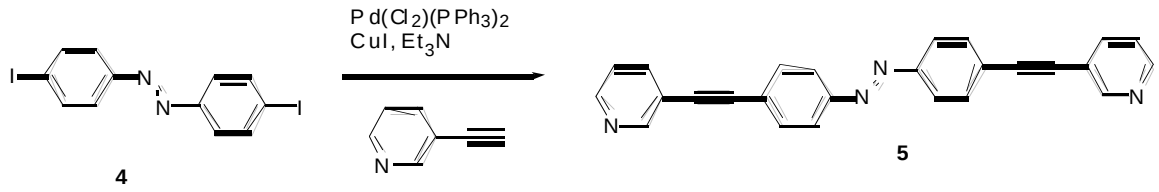
Instrumentation. ^{1}H and ^{13}C NMR spectra were obtained using a Varian Inova 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C), a Varian Inova 300 (300 MHz for ^{1}H), spectrometer, or a Varian Inova 500 (500 MHz for ^{1}H) spectrometer. Chemical shifts are reported in ppm relative to residual non-deuterated solvent. UV-visible absorption spectra were obtained at (21 ± 1) °C using an Agilent 8453 spectrophotometer. Fourier-transform infrared (FT-IR) spectra were recorded using a Mattson Satellite FT-IR spectrometer. The FT-IR samples were prepared as thin films on Ge crystals. Powder X-ray diffraction (XRD) profiles were obtained using an Inel CPS 120 diffraction system (Cu K_α radiation) equipped with a programmable capillary oven. Polarized light optical textures were obtained using a Leica DMRXP microscope equipped with a programmable Linkam THMSE 600 hot/cold stage and an

Optronix digital camera. A Shark series 375 nm UV-LED (OTLH-0280-UV) from Opto Technology, Inc. (driven at 250 mA) was used to irradiate the samples with UV light. Visible light irradiation was performed using the 470 nm UV-LED (OTLH-0010-BU) from Opto Technology (driven at 300 mA). The minimized structure of **1b** was calculated using Cache Ab Initio software (version 6.1.12.33), a semi-empirical PM5 calculation.



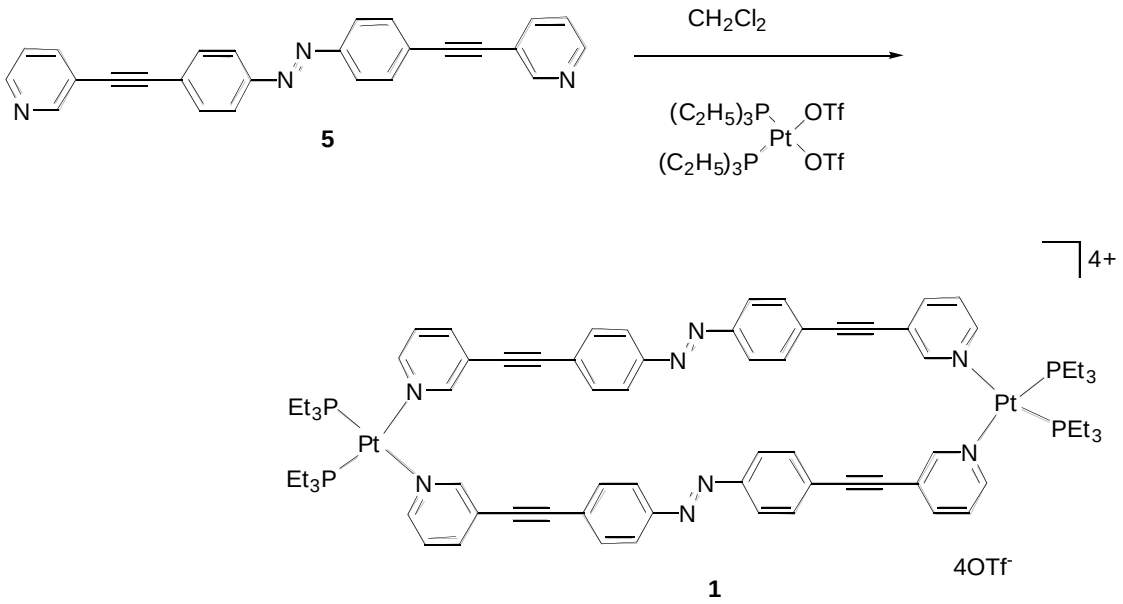
Scheme S1. Synthesis of azobenzene bridge unit **4.**

Bis-(4-iodo)-azobenze (4).[1]. The synthesis of this compound is outlined in Scheme S1: 4-Iodoaniline (3.1 g, 14 mmol) and ^{t}BuOK (3.5 g, 36 mmol) were added to a 1000-mL round-bottom flask containing a magnetic stirbar, followed by 500 mL of an 80/20 (v/v) mixture of DMSO/^{t}BuOH. O_2 was bubbled through this mixture for 2 h with stirring, during which time an orange precipitate formed. The mixture was then filtered through a fritted funnel and washed successively with methanol (50 mL), water (50 mL), and methanol (50 mL). The orange powder was dried in vacuo to yield 1.5 g (48%) of the desired product. Spectral data agreed with those reported in the literature.[2]



Scheme S2. Synthesis of azobenzene bipyridine ligand **5.**

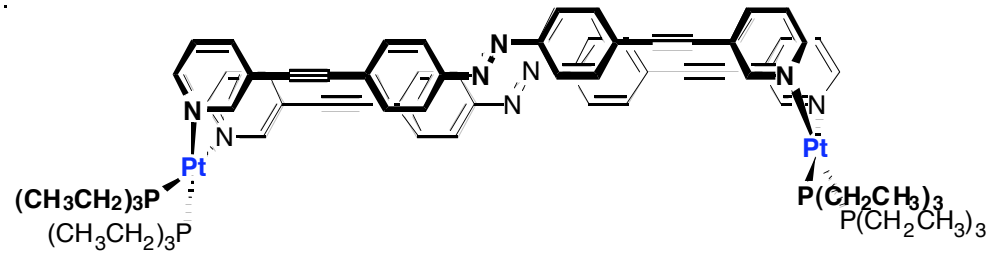
Bis-(4-pyridin-3-ylethynyl)-azobenzene (5).[1] The synthesis of this compound is outlined in Scheme S2: To a Schlenk flask charged with **4** (1.05 g, 2.40 mmol) was added 3-ethynylpyridine (0.52 g, 4.8 mmol), copper(I) iodide (23 mg, 0.12 mmol), $PdCl_2(PPh_3)_2$ (84 mg, 0.12 mmol), triphenylphosphine (50 mg, 0.20 mmol), and triethylamine (25 mL). The mixture was heated to 60 °C and stirred for 16 h under argon at this temperature. After cooling to ambient temperature, the solvent was removed in vacuo, and the mixture was chromatographed over silica gel using CH_2Cl_2 with gradient elution of EtOAc (increasing concentration from 0 to 50% by volume) to give the product as an orange powder after solvent removal in vacuo. Yield: 350 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, 2H) 8.57-8.55 (dd, 2H), 7.94-7.92 (m, 4H), 7.84-7.81 (m, 2H), 7.69–7.67 (m, 4H), 7.31–7.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 152.3, 149.1, 132.8, 125.7, 123.4, 120.3, 92.5, 88.8. IR (cm^{-1}): 453, 564, 701, 724, 800, 852, 1020, 1108, 1153, 1186, 1284, 1405, 1492, 1557, 1594. HRMS $[M + H]^+$ calcd: 385.1447, found: 385.1435.



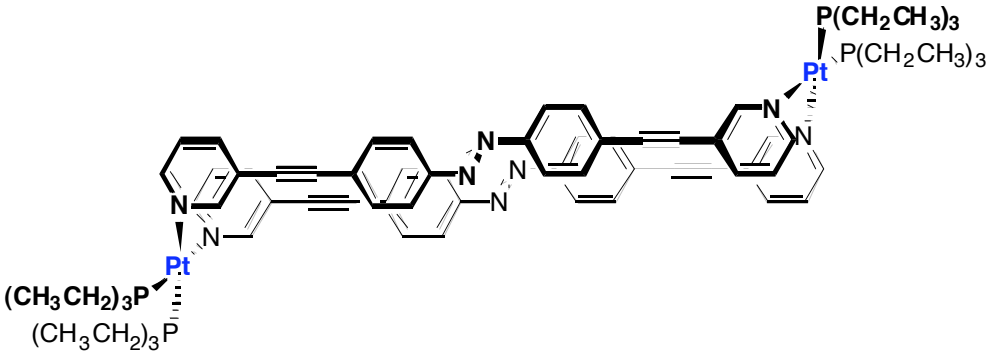
Scheme S3. Synthesis of macrocycle **1.**

Azobenzene macrocycle (1).[1] The synthesis of this compound is outlined in Scheme S3: Into a 25-mL round-bottom flask was added a magnetic stirbar and equimolar amounts of **5** (14.4 mg, 0.0380 mmol) and $Pt(PEt_3)_2(OTf)_2$[2] (26.4 mg, 0.0380 mmol) with dichloromethane (5 mL). The reaction mixture was initially turbid due to the poor solubility of **5** in dichloromethane but became clear red over the course of 6 h with stirring at ambient temperature. Diethyl ether was added to precipitate **1** as red precipitate, and then the precipitate was washed with cold dicholoromethane (5 mL). Yield: 40 mg (99%). X-ray quality crystals of **1** in the all-*trans* form can be grown by the slow vapor diffusion of diethyl ether into a nitromethane solution of **1**. The all-*trans* "boat-like" conformer of **1** (isomer **1a**) is crystallized preferentially. ^{1}H NMR (400 MHz, acetone-d_6): δ = 9.77, 9.75 (s, s 4H), 9.22, 9.20 (s, s 4H), 8.27-8.25 (m, 4H), 7.85–7.71 (m, 20H), 2.82-2.14 (m, 24H) 1.45–1.37 (m, 36H). ^{13}C NMR (125 MHz, acetone-d_6): δ = 152.6, 152.3, 149.2, 138.8, 132.8, 125.7, 123.4, 123.3, 120.3, 92.5, 88.8. ^{31}P (162 MHz, acetone-d_6) δ = 10.1 (Pt satellite), 0.4, 0.3, -9.3 (Pt satellite). IR (cm^{-1}): 700, 852, 1019, 1152, 1402, 1491, 1593, 2322, 2329, 2343, 2357. X-ray crystal structure: see attached .cif file.[9]

In solution, there is presumably a "chair-like" conformer of **1a** as well (Fig. S1), according to NMR evidence (Figs. S2 and S3) and NMR studies of similar metal-organic coordination macrocycles.[4] While the azobenzene unit provides additional asymmetry to the boat conformer, only one set of peaks is seen in the ^{1}H and ^{31}P NMR spectra of **1a** in solution, which is likely a result of the small difference in local environment of the respective nuclei. Additionally, the two sets of NMR peaks are nearly equal in integration, indicating that both conformers of **1a** are nearly equal in energy. Calculations support this data, with PM5 single-point energy calculations run on MM3 minimized boat-like and chair-like conformers showing only a difference of 9 kcal/mol between the calculated energies.



Boat-like form of **1a**
(from single crystal X-ray structure)



Chair-like form of **1a**
(from PM5 minimization)

Figure S1. Schematic representations of "boat-like" and "chair-like" conformers of **1a**. NMR evidence suggests that boat-like and chair-like conformers of **1a** exist in solution, but the boat-like conformer crystallizes preferentially. Stang and coworkers[4] have observed similar conformational behavior in solution with related metal-organic coordination macrocycles with pyridine ligands.

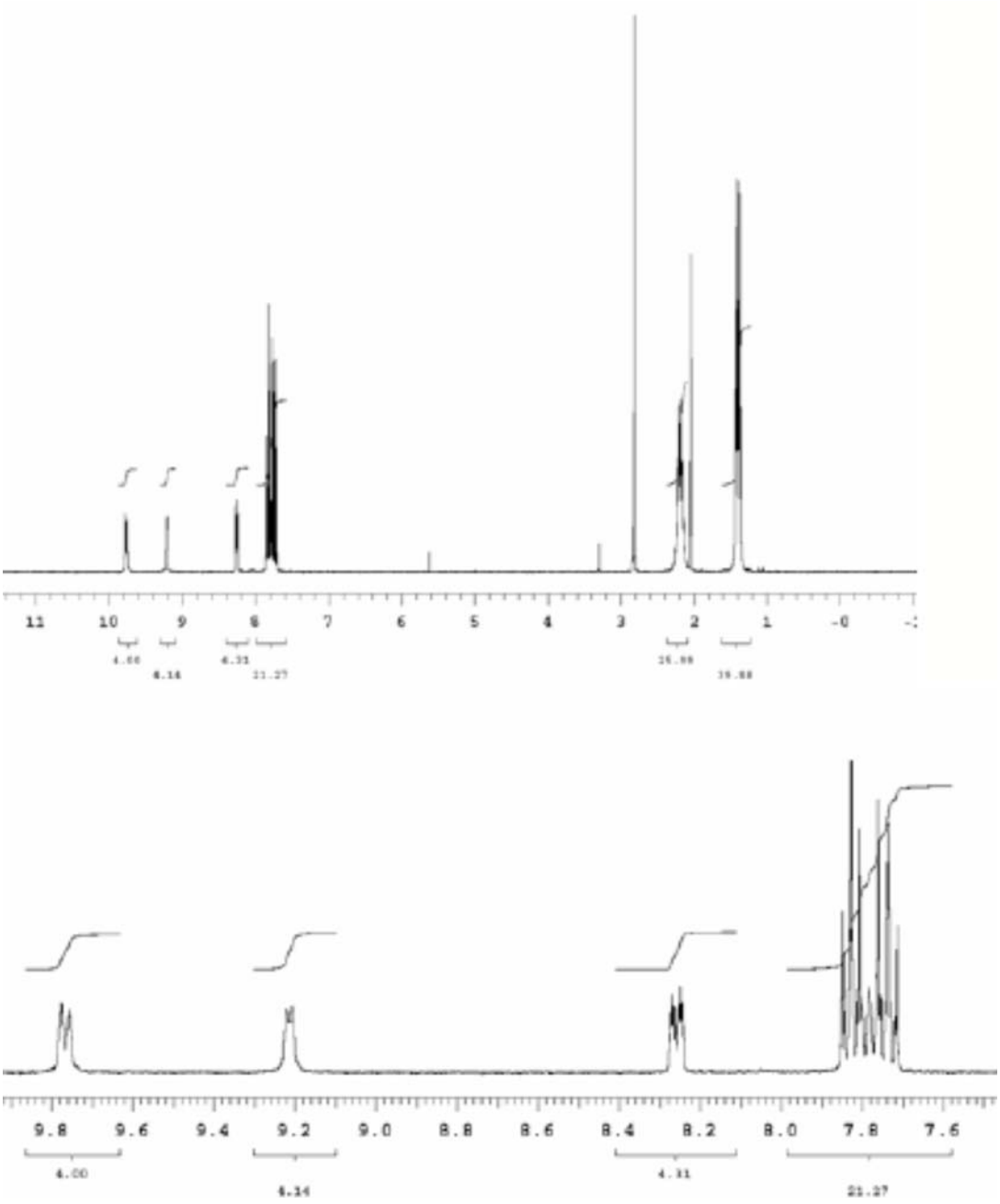


Figure S2. ^{1}H NMR spectra of **1a** (acetone-d_6) showing additional resonances from the chair conformer. Assignment of the additional NMR resonances to the presence of boat-like and chair-like conformers of similar metal-organic macrocycles has been previously established.[4]

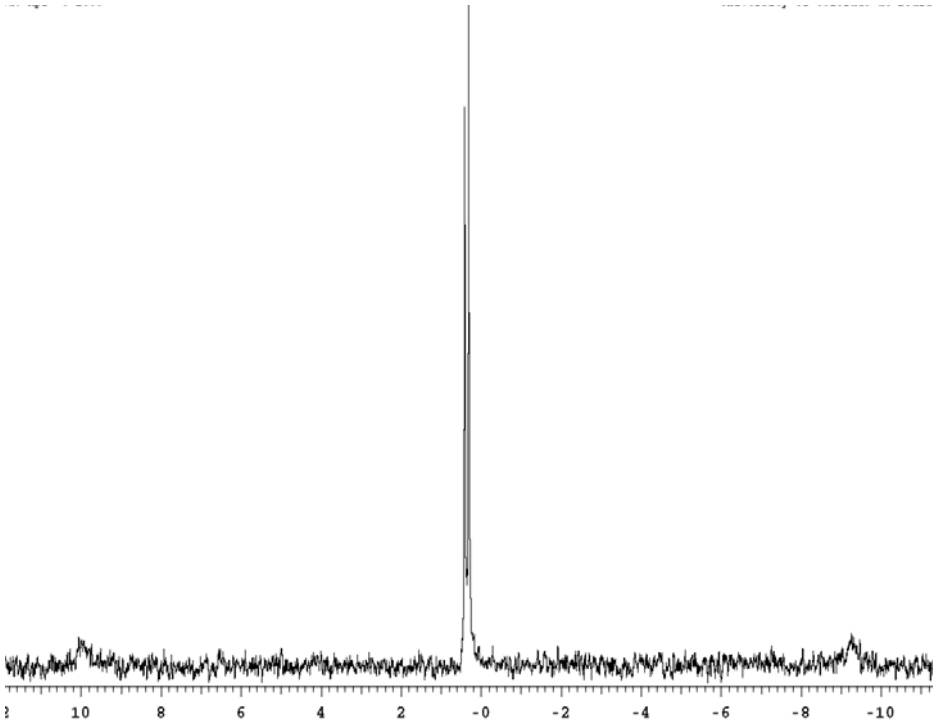
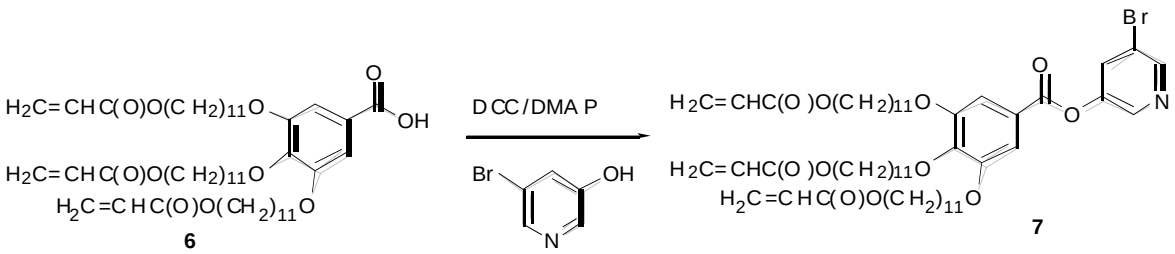


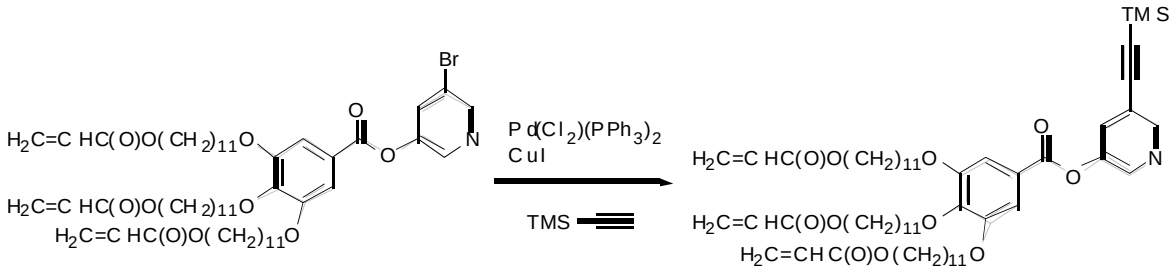
Figure S3. ^{31}P NMR spectrum of **1a** (in acetone-d_6) showing two ^{31}P resonances (with the Pt satellites), which indicates the presence of boat-like and chair-like conformers for metal-organic coordination macrocycles in solution.[4]

3,4,5-Tris-(11-acryloyloxy-undecyloxy)-benzoic acid (6).[4] This compound was synthesized according to literature procedures. Spectroscopic characterization data agreed with those previously reported in the literature.[5]



Scheme S4. Synthesis of polymerizable, wedge-like bromopyridine unit **7.**

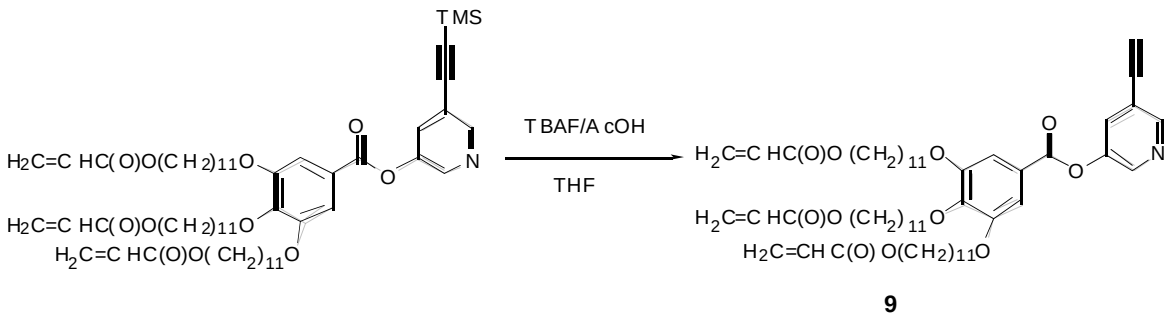
3,4,5-Tris-(11-acryloyloxy-undecyloxy)-benzoic acid 5-bromo-pyridin-3-yl ester (7). The synthesis of this compound is outlined in Scheme S4: To a 25-mL, round-bottom flask equipped with a magnetic stirbar was added **6** (830 mg, 0.980 mmol), 5-bromo-pyridin-3-ol (188 mg, 1.08 mmol), *N,N*'-dicyclohexylcarbodiimide (222 mg, 1.08 mmol), and a catalytic amount of 4-dimethylaminopyridine. A mixture of dicholoromethane and diethyl ether (10 mL, 1:1 (v/v)) was added, and the mixture was stirred for 2 h at ambient temperature. At this time, the urea byproduct was filtered off, and the volatile components removed in vacuo. Silica gel chromatography was performed (4:5 ethyl acetate:hexanes), and product **7** (797 mg, 80%) was recovered after removal of the solvent as a white solid . ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.51 (d, 1H), 7.69–7.68 (m, 1H), 7.39 (s, 2H), 6.42–6.38 (m, 3H), 6.15–6.10 (m, 3H), 5.82–5.80 (m, 3H), 4.16–4.13 (m, 6H), 4.09–4.04 (m, 6H), 1.85-1.82 (m, 4H), 1.78–1.75 (m, 2H), 1.68–1.64 (m, 6H), 1.51–1.47 (m, 6H), 1.43–1.29 (brd, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 164.4, 153.3, 148.2, 147.8, 143.7, 142.1, 132.6, 130.7, 128.8, 122.7, 120.2, 108.9, 73.8, 69.4, 64.9, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 28.8, 26.3, 26.1. IR (cm^{-1}): 668, 1119, 1189, 1272, 1297, 1336, 1407, 1431, 1726, 2327, 2341, 2358, 2854, 2926, 3734. HRMS $[M + Na]^+$ calcd: 1020.4812, found: 1020.4780.



8

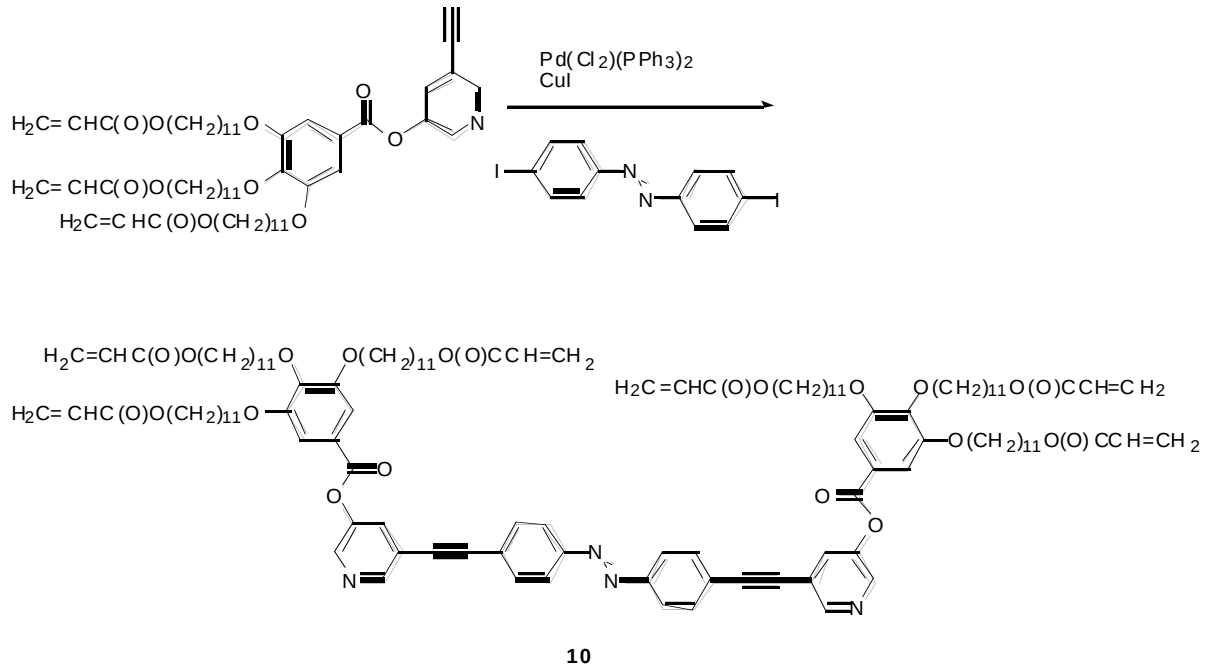
Scheme S5. Synthesis of compound **8.**

3,4,5-Tris-(11-acryloyloxy-undecyloxy)-benzoic acid 5-trimethylsilanylethynyl-pyridin-3-yl ester (8). The synthesis of this compound is outlined in Scheme S5: To a 25-mL Schlenk flask equipped with a magnetic stirbar was added **7** (1.00 g, 1.00 mmol), $Pd(Cl_2)(PPh_3)_2$ (70 mg, 0.10 mmol), copper iodide (19 mg, 0.10 mmol), and triethylamine (10 mL). Trimethylsilylacetylene (245 mg, 2.50 mmol) was then added, and the reaction was left to stir under argon at 80 ºC for 16 h. The volatiles were removed under vacuum, and the residue was purified via silica gel chromatography (ethyl acetate:hexanes, 3:7 (v/v)) to yield a clear oil. Yield: 0.85 g, 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (d, 1H), 8.45 (d, 1H), 7.65–7.64 (m, 1H), 7.37 (s, 2H), 6.42–6.36 (m, 3H), 6.15-6.06 (m, 3H), 5.82–5.78 (m, 3H), 4.16–4.10 (m, 6H), 4.08–4.01 (m, 6H), 1.85–1.63 (m, 12H), 1.48 (brd, 6H), 1.29 (brd, 36H), 0.25 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 164.5, 153.2, 149.9, 147.2, 143.6, 143.1, 132.4, 130.7, 128.9, 123.0, 121.1, 108.8, 100.5, 99.5, 73.8, 69.5, 64.9, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 28.8, 26.3, 26.2, -0.03. IR (cm^{-1}): 855, 986, 1119, 1158, 1190, 1251, 1268, 1296, 1336, 1408, 1432, 1457, 1471, 1506, 1586, 1727, 2855, 2928. HRMS $[M + Na]^+$ calcd: 1038.6102, found: 1038.6090.



Scheme S6. Synthesis of acetylene intermediate **9.**

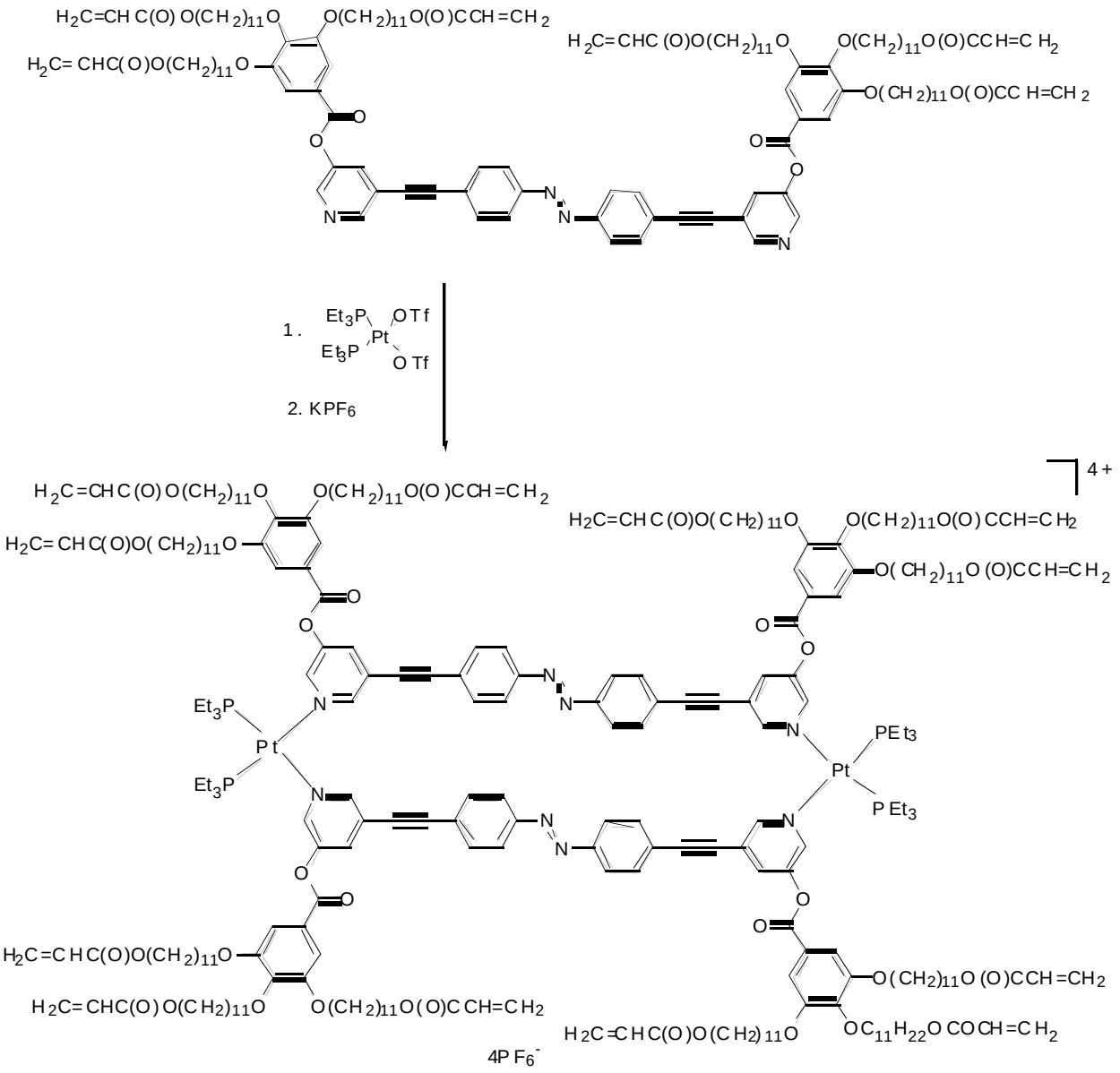
3,4,5-Tris-(11-acryloyloxy-undecyloxy)-benzoic acid 5-ethynyl-pyridin-3-yl ester (9). The synthesis of this compound is shown in Scheme S6: Deprotection of **8** was accomplished by addition of a 1.0 M tetra(*n*-butyl)ammonium fluoride (1.0 mL, 0.90 mmol) solution in THF to a buffered solution of acetic acid (75 mg, 1.2 mmol), **8** (620 mg, 0.616 mmol), and THF (10 mL). Without acetic acid, cleavage of the ester group was observed. After stirring for 0.5 h at room temperature, the solution was poured into water and extracted with dichloromethane (3 x 50 mL). The solvent was then removed in vacuo, and the residue purified by silica gel chromatography using ethyl acetate:hexanes (4:6 (v/v)). Further purification was accomplished by dissolving the product in isopropyl ether and precipitating with hexanes. Yield: 480 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (d, 1H), 8.51 (d, 1H), 7.68–7.67 (m, 1H), 7.39 (s, 2H), 6.43-6.37 (m, 3H), 6.16–6.07 (m, 3H), 5.83–5.80 (m, 3H), 4.17–4.04 (m, 12H), 3.27 (s, 1H), 1.86–1.64 (m, 12H), 1.49 (brd, 6H), 1.30 (brd, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 164.5, 153.2, 150.1, 147.2, 143.7, 143.6, 132.6, 130.7, 128.8, 122.9, 120.1, 108.8, 81.7, 79.5, 73.8, 69.5, 64.9, 60.6, 30.5, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 26.3, 26.2, 26.1. IR (cm^{-1}): 984, 1119, 1155, 1191, 1257, 1272, 1295, 1336, 1408, 1431, 1466, 1586, 1726, 2359, 2854, 2927. HRMS $[M + H]^+$ calcd: 944.5887, found: 944.5901.



Scheme S7. Synthesis of bipyridine compound **10**.

Bis-(3,4,5-Tris-(11-acryloyloxy-undecyloxy)-benzoic acid 5-ethynyl-pyridin-3-yl ester)azobenzene (10). The synthesis of this compound is shown in Scheme S7: Into a 25-mL Schlenk flask equipped with a magnetic stir barstirbar was placed **4** (50 mg, 0.12 mmol), **10** (232 mg, 0.243 mmol), $Pd(Cl_2)(PPh_3)_2$ (8.0 mg, 0.012 mmol), copper iodide (2.0 mg, 0.012 mmol), and triethylamine (5 mL). The mixture was heated to 80 °C under argon for 1 h. The volatile components were then removed under reduced pressure, and the residue was purified by silica gel chromatography using hexanes:ethyl acetate (7:3 (v/v)) to yield the product 10 as a red waxy solid. Yield: 60 mg (60%). 1H NMR (300 MHz, CDCl3): δ = 8.71 (s, 2H), 8.52 (d, 2H), 7.97–7.95 (m, 4H), 7.78 (m, 2H), 7.72–7.69 (m, 4H), 7.41 (s, 4H), 6.43–6.37 (m, 6H), 6.17–-6.07 (m, 6H), 5.84–5.79 (m, 6H), 4.17–4.04 (m, 24H), 1.87–1.74 (m, 12H), 1.71–1.62 (m, 12H), 1.49 (brd, 12H), 1.30 (brd, 72H). 13C NMR (125 MHz, CDCl3): δ = 166.6, 164.5, 153.3, 152.4, 149.5, 147.4, 143.7, 143.2, 132.9, 132.1, 130.7, 128.9, 125.4, 123.4, 122.9, 121.0, 108.9, 93.3,

87.7, 73.8, 69.5, 64.9, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 28.8, 26.3, 26.2, 26.1. IR (cm^{-1}): 810, 983, 1061, 1122, 1154, 1194, 1272, 1297, 1338, 1408, 1431, 1466, 1498, 1587, 1727, 2342, 2359, 2854, 2926. HRMS $[M + H]^+$ calcd: 2066.2223, found: 2066.2273.



Scheme S8. Synthesis of amphiphilic macrocyclic LC monomer **2.**

Amphiphilic bis(azobenzene)-acrylate macrocycle monomer 2. The synthesis of this compound is shown in Scheme S8: Into a 25-mL round-bottom flask was placed compound **10** (100 mg, 0.0504 mmol) and $Pt(PEt_3)_2(OTf)_2$ (49 mg, 0.10 mmol) with dichloromethane (5 mL). The resulting red solution was left to stir at ambient temperature for 2 h. A saturated aqueous solution of KPF_6 (5 mL) was prepared and added to the reaction mixture. The mixture was then stirred for 5 min and subsequently transferred into a separatory funnel. The organic fraction was saved, and this process was repeated. Then the volume of the organic fraction was reduced to ca 1 mL, and isopropyl ether was added to precipitate out a red waxy solid. This solid was then re-suspended in methanol and centrifuged to yield **2** as a red solid. Yield: 101 mg, (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32–9.30 (d, 4H), 8.95–8.93 (d, 4H), 7.93 (s, 4H), 7.74 (s, 8H), 7.65 (s, 8H), 7.33 (s, 8H), 6.40–6.35 (m, 12H), 6.13–6.06 (m, 12H), 5.80–5.77 (m, 12H), 4.14–4.10 (m, 24H), 4.02–3.93 (m, 24H), 2.06–1.91 (m, 24H), 1.77–1.70 (m, 24H), 1.66–1.61 (m, 24H) 1.44 (brd, 24H), 1.30 (brd, 180H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 164.5, 153.3, 152.7, 152.6, 150.0, 149.6, 144.7, 144.0, 135.7, 133.6, 133.5, 130.7, 128.8, 125.6, 124.1, 123.9, 123.2, 121.8, 109.0, 98.4, 98.2, 84.1, 83.9, 73.7, 69.4, 64.9, 30.6, 30.0, 29.9, 29.8, 29.8, 29.7, 29.5, 28.5, 26.3, 26.3, 26.2, 15.8, 7.9. IR (cm^{-1}): 812, 844, 917, 928, 946, 986, 1012, 1036, 1049, 1071, 1118, 1150, 1189, 1239, 1273, 1296, 1337, 1348, 1380, 1408, 1431, 1455, 1487, 1496, 1584, 1725, 2855, 2927, 2974. HRMS $[M\text{-}3PF_6]^{+3}$ calcd: 1713.5651 found: 1713.5706. Fig. S4 below shows HRMS profiles and the isotropic distributions of the 3+ and 4+ ions of monomer **2**.

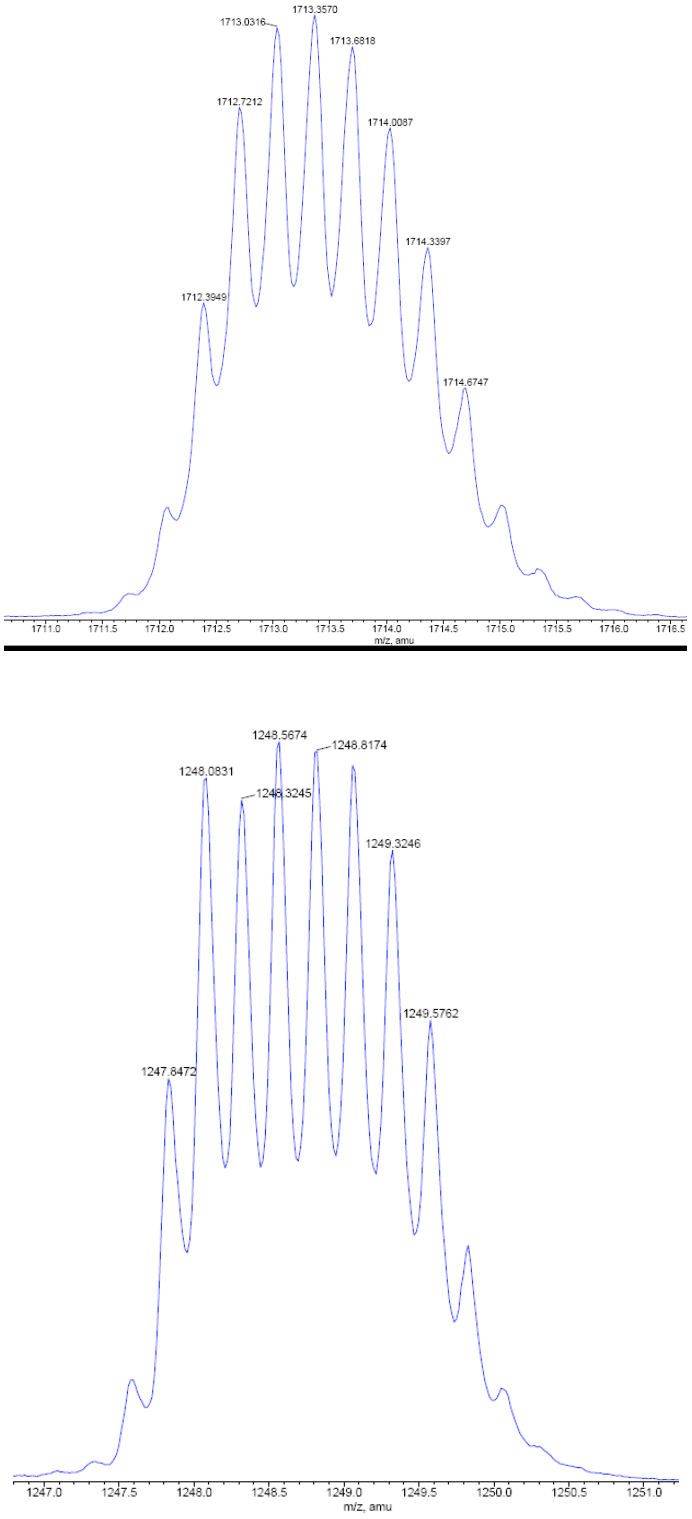


Figure S4. Mass spectra showing the isotopic distribution of the 3+ (top) and 4+ (bottom) ions of **2**.

Photo-isomerization studies of macrocycle 1 in dilute solution. In order to demonstrate the photo-isomerization viability of this macrocycle design, the core molecule **1** in the all–*trans* form **1a** was irradiated with 375 nm light in dilute dichloromethane solution (0.1 mg/mL), and the total amount of *cis* content was calculated by UV-visible spectroscopy. By observing the drop in the intensity of the *trans* azobenzene absorption band at 375 nm (π–π*), the total degree of conversion to *cis* isomers was calculated to reach ca. 80% in dilute dichloromethane solution (Fig. S5).[6] Irradiation of **5** produced essentially similar results. Both **5** and macrocycle **1b** showed reversible formation of the corresponding all-*trans* isomers after exposure to visible light, or by allowing the samples to sit in the dark and relax thermally.

Photo-isomerization studies of macrocycle 1 in concentrated solution. In order to confirm the degree of *trans* to *cis* photo-isomerization determined by the UV-visible spectral analysis, more concentrated solutions (5 mg/mL) in deuterated acetone were prepared and analyzed by ^{1}H NMR spectroscopy. Upon irradiation of **1a** (for 24 h), new ^{1}H peaks corresponding to what are presumably the *cis-cis* (**1b**) and mixed *cis-trans* (**1c**) isomers of **1** become visible in the ^{1}H NMR spectra (Fig. S6). The protons associated with *trans*-azobenzene undergo a significant upfield shift upon conversion to the *cis* isomer and are readily identifiable.[7] Indeed, there are two new pairs of NMR resonances due to the presence of *cis*-azobenzene that can likely be assigned to the *cis-cis* (**1b**) and *cis-trans* (**1c**) isomers. Integration of these 1H NMR peaks can be compared to that from the *trans*-isomer, and the total *cis* content can be calculated and compared to that obtained from UV-visible absorption data: *Cis* isomer conversion by ^{1}H NMR integration: 55%. *Cis* isomer conversion calculated from UV-visible spectroscopy: 51 %. Also shown in Fig. S6 is clean, quantitative relaxation to the *trans* isomer after 24 h of sitting in ambient light, indicating that no other irreversible photochemical processes were occurring during irradiation.

Possible photo-isomeric and conformation forms of the bis(azobenzene) macrocyclic compounds 1 and 2 in solution and the LC state. The boat-like all-*trans* isomer of macrocycle **1** (isomer **1a**) is crystallized preferentially as a ground state compound. However, it should be noted that boat-like and chair-like conformers of all the three photo-isomeric forms of the bis(azobenzene) macrocyclic compounds **1** and **2** (*trans-trans*, *cis-cis*, and partially isomerized mixed *cis-trans* isomers) could exist in solution or the LC state. This means that during the photo-isomerization experiments, there may be up to 6 discrete conformational photo-isomeric forms of **1** or **2** present. The identities and relative abundances of all these isomers and conformational forms would be very difficult to determine using typical spectroscopic techniques given their similar molecular structures. Undoubtedly this would lead to complexity in spectral characterization, and exact identification and isomer/conformer abundance determination may not viable. UV-visible and NMR analyses only allow facile determination of the total amount of *trans* and *cis* azobenzene units present because of their very different absoprtion maxima and chemical shift environments, but not facile identification of the very similar isomeric/conformation forms. Although we cannot definitively ascertain the presence of boat-like and chair-like conformers for every *cis*-containing azobenzene intermediate, these conformers likely further complicate the mixture, and in this thermodynamically controlled system, their relative proportions would depend on their energy. It should be noted that detailed photo-isomerization behavior of these metal-coordination azeobenezene macrocycles is NOT the goal of this research. The main goal of this research is demonstrating that photo-isomerization-based macrocycle size changes can be induced in a LC polymer system with retention of order, as a means of performing nanopore size gating.

Studies confirming the structural integrity of azobenzene coordination macrocycle 1 and compounds based on 1. Given the weak and reversible nature of the Pt-pyridine coordination bonds, there is some question as to the stability of the macrocycle **1a** after photo-isomerization to **1b**, (and by analogy, the stability of the all-*trans* form of monomer **2** after

photo-isomerization, as well.) However, ^{1}H NMR studies of irradiated samples show no signs of the free azobenzene ligand (compound **5**) in solution (Fig. S6), indicating that the macrocycle **1a** is intact in the more open *cis* form **1b**. It should be noted that photo-conversion of **1a** to **1b** is not complete—^{1}H NMR resonances can be observed that correspond to the *trans-trans* (**1a**), *trans-cis* (**1c**), and *cis-cis* (**1b**) isomers in the solution after UV light irradiation (Fig. S6).

Also the all-*trans* isomer **1a** is stable when stored in concentrated acetone-d_6 solution for a week at ambient temperature, with no change in the ^{1}H NMR profile over the storage time. Monomer **2** was also found to have an excellent shelf-life when stored in concentrated dichloromethane solution or as a solid.

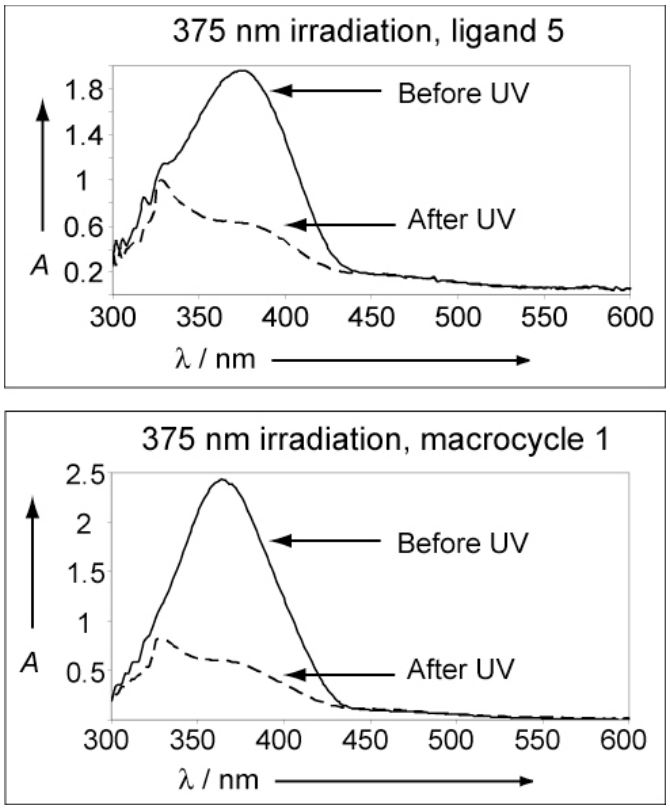


Figure S5. UV-visible absorption spectra showing the degree of photo-conversion to the *cis* isomer for the free azoebenzene ligand **5** (top spectrum), and macrocycle **1** (bottom spectrum), by irradiation with 375 nm light.

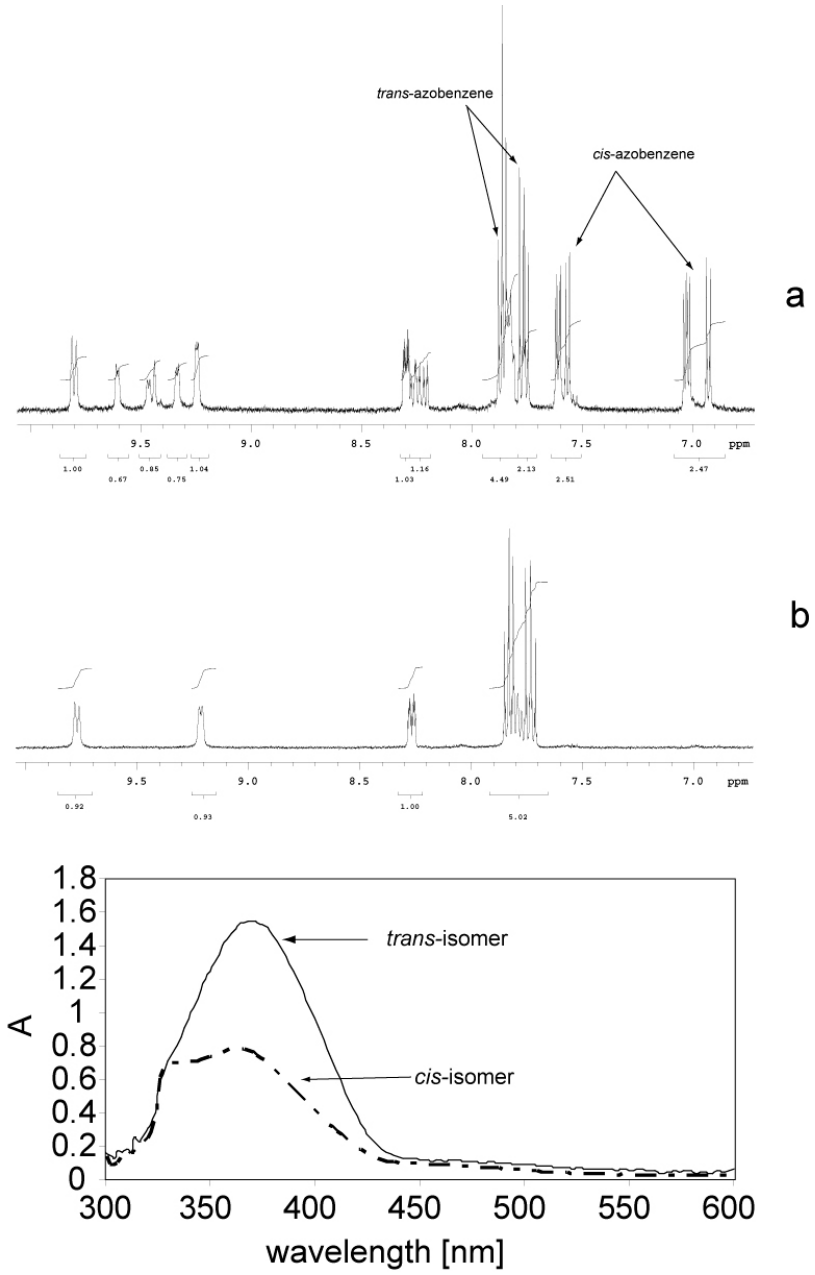


Figure S6. ^{1}H NMR spectrum of macrocycle **1** (a) after irradiation with 375 nm light; and (b) after thermal relaxation of for 24 h. The UV-visible absorption spectra of the pre- and post-UV irradiation samples are shown below the NMR spectra. No trace of free ligand **5** in the ^{1}H NMR spectrum after photo-isomerization indicates that the macrocycle is intact. Additional peaks indicate a mixture between *trans-trans, trans-cis,* and *cis-cis* isomers. The calculation of the *cis-*

isomer content from UV-visible spectral data on the irradiated solution is in agreement with that calculated by ^{1}H NMR integration (51% vs. 55%, respectively).

Studies showing the importance of added polar solvent to the photo-isomerization of monomer 2. Without added solvent, the photo-isomerization of the all-*trans* form of **2** to the all-*cis* and mixed *cis-trans* isomers of **2** is only marginally successful. Irradiating films of neat **2** in the thermotropic LC Col_H state only results in ca. 10% total photo-conversion to the *cis* isomers (Fig. S7 below). This is likely due to the highly condensed nature of this LC phase and the lack of "free volume" for the molecular expansion upon photo-isomerization of the macrocycle core. Adding 50 wt. % diglyme, a high boiling, polar solvent that solvates the "core" of the macrocycle well, serves to increase the conversion to the *cis* isomers nearly 4-fold (see Fig. 2 in the main manuscript). Presumably, the partial solvation of the ionic core effectively increases the free volume available for the formation of the *cis* isomers and for the core to open. Supporting this hypothesis is an observed corresponding decrease in viscosity in the solvent-swollen Col_H phase.

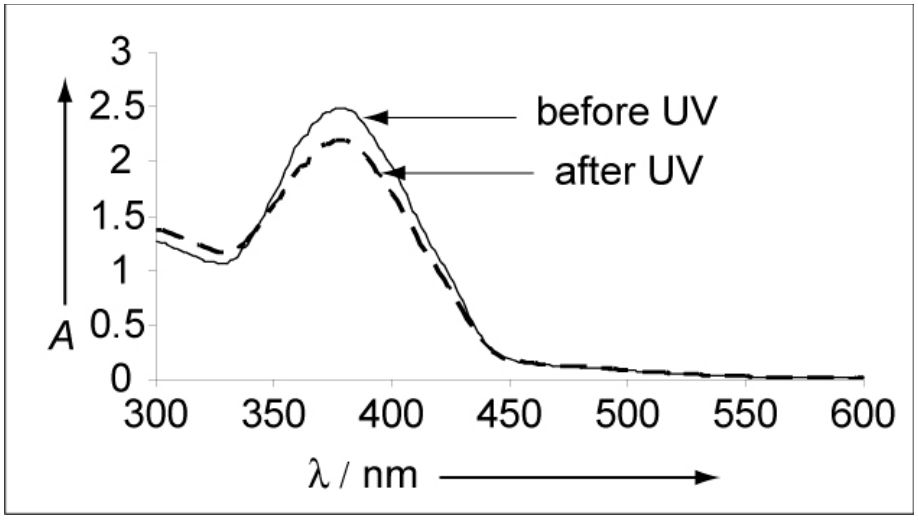


Figure S7. Thin film of **2** (neat) before and after irradiation with 375 nm light.

Radical cross-linking of 2 in the solvent-swollen Col_H state with retention of LC order. AIBN (4 wt %), a thermally activated radical initiator, was added to diglyme. After dissolution, an equal amount by weight of the diglyme/AIBN solution and **2** were mixed together by hand with a spatula until the mixture appeared uniform under the PLM. A small amount of this stock mixture (~1 mg) was then placed between glass microscope slides and pressed by hand to obtain a thin film transparent enough to be analyzed by UV-visible and IR spectroscopy, and by PLM to confirm formation of the desired LC phase. The glass slides were then heated at 60 °C for 2 h in air to initiate the radical cross-linking process. During the radical polymerization process, the film showed no change in optical texture as observed by PLM, other than some shrinkage of the polymer sample during polymerization resulting in "cracks" along the film. After polymerization, the slides were carefully separated and the resulting solid polymer film washed with acetone to remove any residual monomer. IR experiments on the resulting film were performed to determine the degree of acrylate conversion. The degree of thermal radical polymerization was measured to be 40–50% by monitoring the loss in intensity of the acrylate =C–H twist band at ca. 810 cm^{-1} and using the nearby Pt-py stretch at 844 cm^{-1} as a internal reference (Fig. S8).[8] Powder XRD data was also obtained on the cross-linked film (Fig. 4c in the main manuscript) and confirmed retention of most of the Col_H LC structure after thermal radical cross-linking. Before performing azobenzene photo-isomerization experiments, the polymer film was sandwiched between two glass coverslips, with excess diglyme added to wet and swell the polymer.

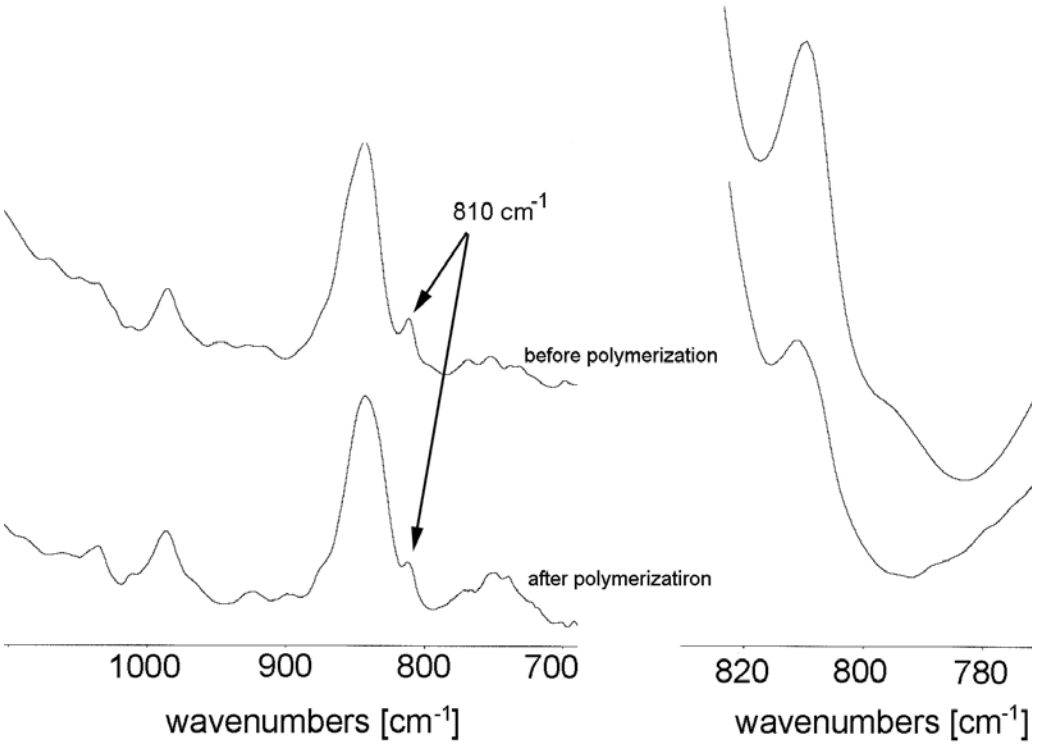


Figure S8. IR absorbance spectra showing the disappearance of the acrylate terminal =C–H twisting band at 810 cm^{-1}.

Preliminary studies demonstrating initial proof-of-concept for differential molecular uptake upon "nano-gating" or "nano-valving" characteristics of polymerized LC films. A depletion method was used to show the effect of the "nano-gating" or "nano-valving" characteristics of the cross-linked lyotropic LC film of **2** on molecular uptake. Thin polymer diglyme-swollen films of monomer **2** were prepared. The films were first washed and soaked in acetone and dioxane to remove any unreacted monomer and photo-initiator. Then, 0.5 mg of the film was then placed in an air-tight (screw-top), quartz, UV-visible spectrophotometer sample cell. 2.5 mL of 10 mg/L of the anionic dye molecule, 3-nitrobenzylsulfonic acid sodium salt (3-NBSA), in dioxane + 0.5 wt. % deionized water was then added to the cell. 3-NBSA has a characteristic UV-visible absorption peak at 261 nm. This particular anionic dye was chosen for this differential uptake experiment because of its ability to anion-exchange with monomer **2**, its

high absorptivity coefficient, and its lack of adsorption around 375 nm. The cell was then immediately sealed, and the polymer film was allowed to soak in the dye solution at ambient temperature. UV-visible absorption spectra of the supernatant dye solution were then taken at 15 min intervals for ca. 17 h. The cell containing the sample film and dye solution was then exposed to 375 nm light (300 mW/cm^2) for the next 30 h while taking periodic measurements. [It should be noted that the dioxane/water solutions of 3-NBSA should be prepared with fresh dioxane (i.e., from a new unopened bottle), stored with minimum exposure to atmospheric O_2, and tested as quickly as possible. The presence and formation of peroxides in the dioxane can lead to significant degradation of the dye upon UV irradiation for extended periods of time.]

The amount of dye ions exchanging with the PF_6^- counter-ions of cross-linked **2** was determined by monitoring the decrease in the intensity of the UV absorption peak centered at 261 nm. Initially, the concentration of the anionic dye decreased to some degree due to ion-exchange and uptake with the surface of the polymer film of **2** in its resting-state closed macrocycle form (Fig. S9, left side of vertical line). The dye concentration decreased from 10.0 mg/L to a steady-state concentration of 7.7 mg/L. This corresponds to 6.3% of the original PF_6^- counter-ions in the Col_H polymer film of **2** (based on mass) exchanging with the anionic dye in solution, giving a value for the background ion-exchange/uptake level possible with the closed macrocycle form of the LC polymer. After the sample film was subjected to ca. 30 h of prolonged UV (375 nm) light exposure (the onset of UV exposure is given by the vertical line in Fig. S9) (thereby opening ca. 30% of the macrocycle units (see main paper)), a significant additional decrease in the supernatant 3-NBSA concentration was observed. The final steady-state dye concentration after UV irradiation was 6.5 mg/L.

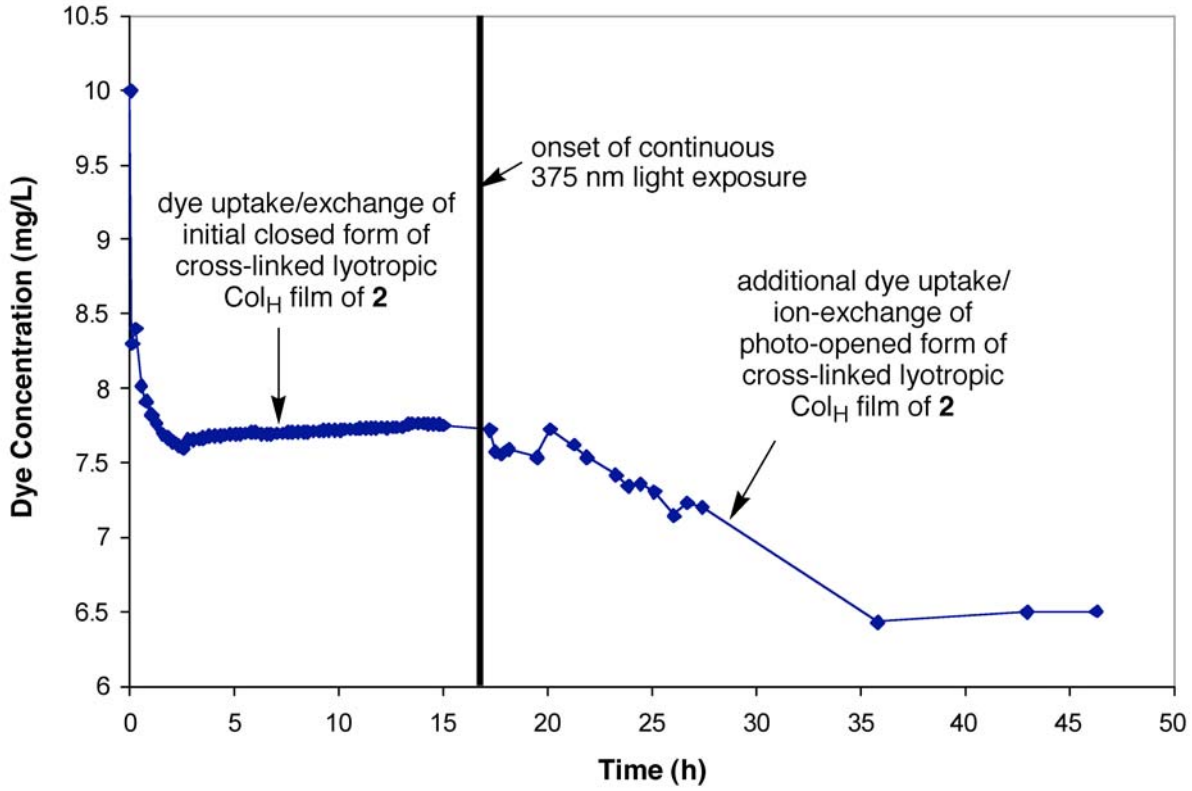


Figure S9. Plot of the decrease in the supernatant solution concentration of 3-NBSA as a functional of time, before and after UV light exposure to photo-isomerize ca. 30% of the bis(azobenzene) macrocycles into the more open form.

It has been reported in literature that 3-NBSA is relatively UV stable in the absence of a photocatalyst over several days.[10, 11] Control experiments with a pristine 10.0 mg/L solution of 3-NBSA irradiated with the same intensity of 375 nm UV light for the same amount of time, showed only a small amount of photo-degradation by UV-vis analysis. There was only a 0.5 mg/L loss of 3-NBSA in the control solution of 3-NBSA due to UV photo-degradation. This means that a *net* additional concentration decrease of 0.7 mg/L after UV irradiation was caused by dye uptake/anion exchange to newly exposed sites in the photo-opened form. This represents an additional dye uptake of 30% compared to the initially all-closed form of the macrocycle LC polymer sample. Thus, it can be inferred that the large anionic dye molecules are more able to

pass through or enter and exchange with the photo-opened macrocycle "nano-gates" on the surface, and perhaps even penetrate more into the bulk film. This initial differential molecular uptake experiment provides proof-of-concept for the LC polymer samples of **2** having responsive "nano-gating" or "nano-valving" properties.

References for Supporting Information:

[1] E. Karp, C. S. Pecinovsky, M. J. McNevin, D. L. Gin, D. K. Schwartz, *Langmuir* **2007**, *23,* 7923.

[2] Y. Z. Li, J. P. Kirby, M. W. George, M. Poliakoff, G. B. Schuster, *J. Am. Chem. Soc*. **1998**, *110*, 8092.

[3] P. J. Stang, D. H. Cao, *J. Am. Chem. Soc*. **1994**, *116*, 4981.

[4] K. Chi, C. Addicott, A. M. Arif, N. Das, P. J. Stang, *J. Org. Chem*. **2003,** *68*, 9798.

[5] R. C. Smith, W. M. Fischer, D. L. Gin, *J. Am. Chem. Soc*. **1997**, *119*, 4092.

[6] W. R. Brode, J. H. Gould , G. M. Wyman, *J. Am. Chem. Soc*. **1952**, *74*, 4641.

[7] L. S. Lever, M. S. Bradley, C. S. Johnson, Jr. *J. Magn. Reson*. **1986,** *68*, 335.

[8] D. Lin-Vien, N. B. Colthup, W. G. Fateley, J. G. Grasseli, in *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Boston, **1991**; Chapter 9.

[9] *CCDC 646228 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.*

[10] A. Alif, P. Boule, J. Lemaire, *J. Photochem. Photobiol. A* **1990** *50*, 331.

[11] A. Rachel, M. Sarakha, M. Subrahmanyam, P. Boule, *Appl. Catal. B*: *Environ*. **2002**, *37*, 293.