Supporting Information for

[2 x 2] Metallo-supramolecular grids based on 4,6-bis((1*H*-1,2,3-triazol-4-yl)-pyridin-2-yl)-2-phenylpyrimidine ligands: From discrete [2 x 2] grid structures to star-shaped supramolecular polymeric architectures

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Experimental section

S1: Materials and Methods

Materials

Unless otherwise stated, all chemicals and solvent were commercially available and used as received. Dichloromethane (DCM, 99.8%), pentane (99.8%), diethyl ether (99.8%), tetrahydrofuran (THF, 99.9%), ethyl acetate, extra dried *N,N*-dimethylfomamide (DMF,99.8%), *n*-butyl lithium (*n*-BuLi) , tetra-*n*-butylammonium fluoride (TBAF), tri-*n*-butyltin chloride (Bu_3SnCl) and triethylamine (Et_3N, 99.5%) were received from Sigma-Aldrich. 4,6-dichloro-2-phenylpyrimidine, 2,6-dibromopyridine, (triisopropylsilyl) acetylene, sodium ascorbate and copper sulfate were purchased from TCI. The silicone grease was purchased from Kurt Obermeier GmbH & Co. KG. Purification of the reaction products was carried out by column chromatography using silica gel or neutral Al_2O_3 90 standardized. Azido-functionalized oligoethylene glycol (Mn = 350 g/mol) was synthesized according to the reported literature.[1] Preparative size exclusion chromatography was performed on Biobeads SX-1 obtained from BIO-RAD company. The solvent used in this report is degassed by purging composed of an argon through the solvent for 30 min prior to use.

Instrumentation

^1H NMR and ^{13}C NMR spectra were performed on a Bruker FT-NMR spectrometer in $CDCl_3$ operating at 300 MHz (^1H) and 101 MHz (^{13}C). The chemical shifts (δ) were reported in ppm related to TMS.

Size-exclusion chromatography (SEC) was performed on an Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler, a thermostatted column compartment, a 1260 diode array detector

(DAD) and a 1260 refractive index detector (RID). Analyses were performed on two Mixed-D (Agilent) 30 cm columns and a Mixed-D precolumn (Agilent) in series at 50 ^{o}C. DMA containing 50 mM of LiCl was used as eluent at a flow rate of 0.5 mL min^{-1}. The spectra were analyzed using the Agilent Chemstation software with the GPC add on. Molar mass and dispersity (Đ) values were calculated against PMMA standards.

Fourier-transform Infrared (FT-IR) spectra were measured using PerkinElmer Frontier FT-IR (midIR) combined with a MKII Golden Gate set-up equipped with a diamond crystal from Specac. The spectra were measured with a wavenumber window between 4000 and 600 cm^{-1}. The material was placed on the measuring plate and the crystal was brought into contact with the dry powder.

MALDI-TOF MS analysis were performed on a STR MALDI-TOF mass spectrometer equipped with 2 m linear and 3 m reflector flight tubes and a 355 nm Blue Lion Biotech Marathon solid state laser (3.5 ns pulse) was used. All mass spectra were obtained with an accelerating potential of 20 kV in positive ion mode and in either reflectron or linear mode. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (20 mg/ml in acetone) was used as matrix and NaTFA (2 mg/ml in acetone) was used as cationizing agent. Polymer samples were dissolved in acetone (2 mg/ml). Analyte solutions were prepared by mixing 10 µl of the matrix solution and 5 µl of the polymer solution, with or without 5 µl of the salt solution. Subsequently, 0.5 µl of this mixture was spotted on the sample plate, and the spots were dried in air at room temperature. A poly(ethylene oxide) standard (Mn = 2000 g/mol) was used for calibration. All data was processed using the Data Explorer 4.0.0.0 (Applied Biosystems) software package.

UV−vis spectra were measured with a Cary 100 Bio UV-Visible spectrophotometer equipped with a temperature controller. The spectra analysis was performed in the 200-

800 nm range at 25 ^{o}C. To a quartz UV-cuvette was added a stock solution (3.0 ml) of the macroligand in acetonitrile. Then 25μL of a stock solution of metal in acetonitrile were added stepwise to the solution and the mixture was shaken. After each addition, the UV-vis spectrum was recorded.

For the structure of **3**, X-ray intensity data was collected at 100 K, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and CuKα (λ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro.[2] Using Olex2,[3] the structure was solved by direct methods using the ShelXS structure solution program and refined by full-matrix least-squares on F^2 using the ShelXL program package.[4, 5] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups).

Synthesis and characterization of the products

2-Bromo-6-[(triisopropylsilyl)ethynyl]pyridine (1)

2,6-Dibromopyridine (5 g, 21.11 mmol), (triisopropylsilyl) acetylene (1.6 mL, 7.03 mmol), $PdCl_2(PPh_3)_2$ (309.53 mg, 0.44 mmol) and CuI (186.64 mg, 0.98 mmol) were suspended in 40 mL degassed THF and 5 mL of degassed NEt_3. The reaction was stirred for 2 h at room temperature and filtered. The solvents were evaporated, and the residue was purified by column chromatography on silica (eluent *n*-pentane/CH_2Cl_2) to give **1** (1.657 g, 4.9 mmol) as a colorless oil (69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 3H, pyridine-H), 1.13 (s, 18H, –Si-(CH- $(CH_3)_2)_3$), 1.12 (s, 3H –Si-(CH-$(CH_3)_2)_3$). The spectral data was identical to those reported in literature.[6]

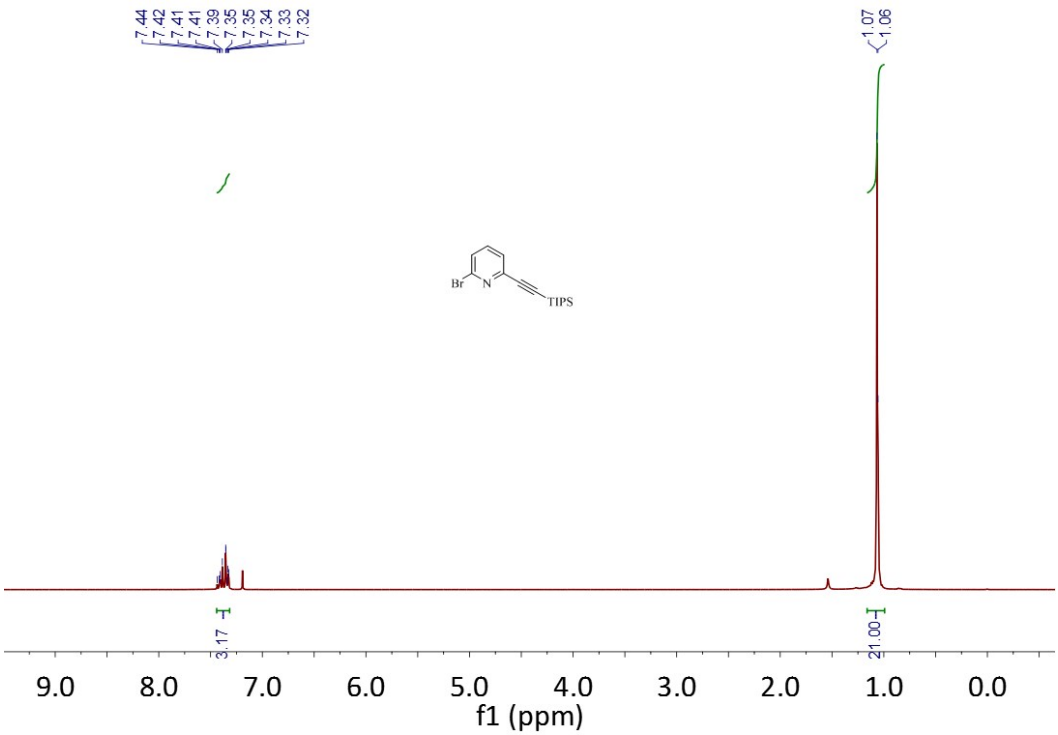


Figure S1. ^{1}H-NMR spectrum of 2-bromo-6-[(triisopropylsilyl)ethynyl]pyridine in $CDCl_3$.

2-[(Triisopropylsilyl)ethynyl]-6-(tributylstannyl)pyridine (2)

1(1g, 2.96 mmol) was dissolved in 50 mL of extra dry THF. To this was added *n*-BuLi (1.42 mLof 2.5 M solution in hexane, 3.55 mmol) dropwise at -78 ^{o}C. Once the addition was completed, the reaction was allowed to warm to -20 ^{o}C and then was cooled again to -78 ^{o}C. A 5 ml of THF solution of Bu_3SnCl (1.2 mL, 4.08 mmol) was then added dropwise. After completing the addition, the reaction was allowed to warm to room temperature and stirred overnight under argon. After the reaction, the solvents were evaporated and the residue was purified by column chromatography on Al_2O_3 with *n*-pentane as eluent to give **2** (680.58 mg, 1.239 mmol) as a colorless oil (42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.4, 6.7 Hz, 1H), 7.29 (d, J = 7.4 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 1.60 – 1.51 (m, 6H), 1.33 (m, 6H), 1.15 (s, 18H), 1.14 (s, 3H) 1.13 –

1.07 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). The spectral data was identical to those reported in literature.[6]

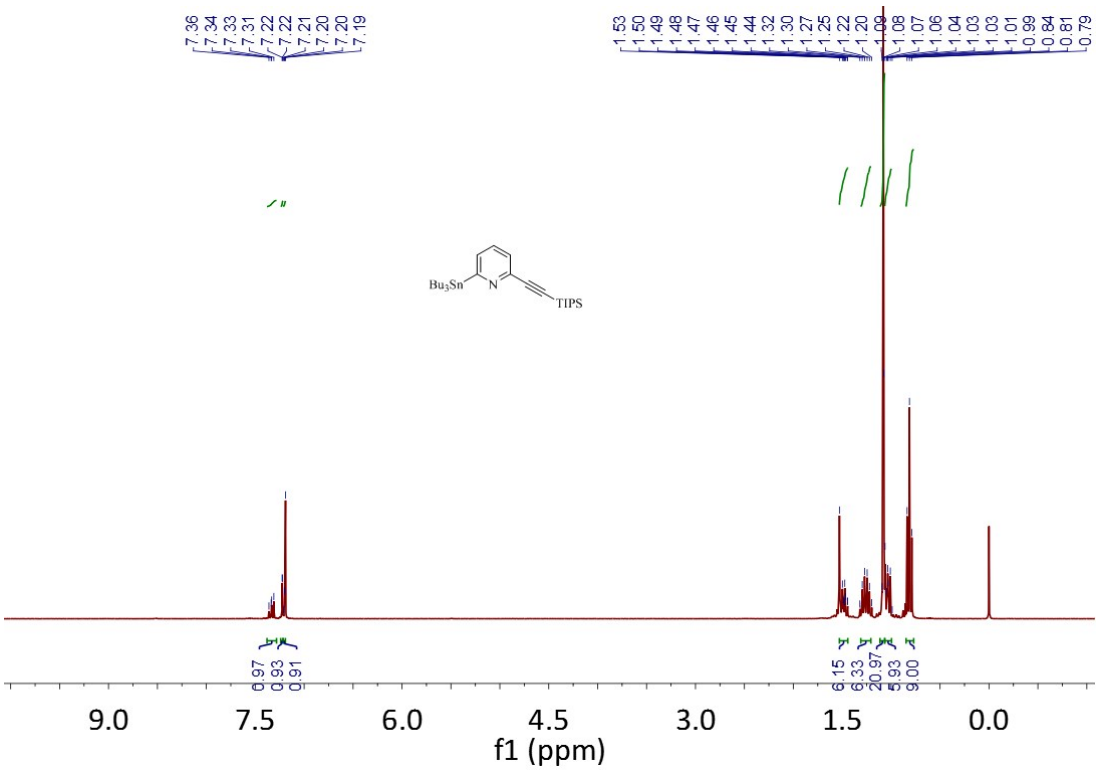
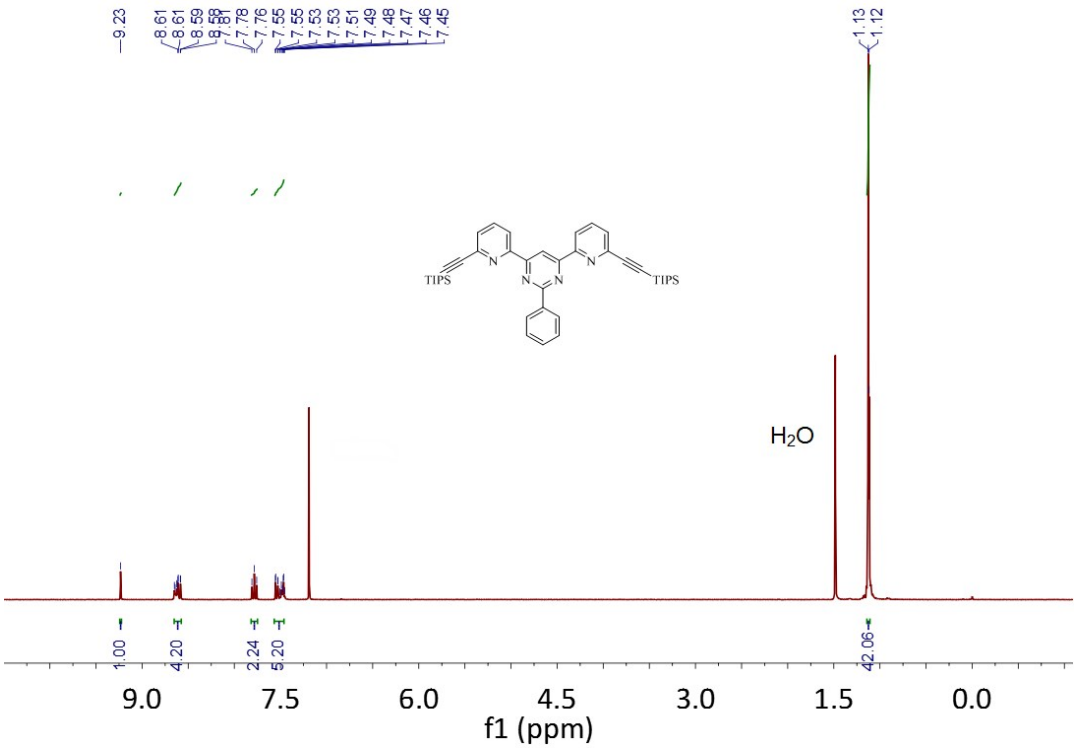


Figure S2. ^{1}H-NMR spectrum of 2-[(triisopropylsilyl)ethynyl]-6-(tributylstannyl)pyridine in $CDCl_3$.

2-Phenyl-4,6-bis(6-((triisopropylsilyl)ethynyl)pyridin-2-yl)pyrimidine (3)

2 (1 g, 1.82 mmol), 4,6-dichloro-2-phenylpyrimidine (163.12 mg, 0.73 mmol) and $PdCl_2(PPh_3)_2$ (84.32 mg, 0.073 mmol) were brought in a dry round bottom flask and 10



ml of dry DMF was added. The mixture was stirred under an argon atmosphere at 80°C for 42 hours. The solvents were evaporated and the residue was purified by column chromatography on silica with *n*-pentane/DCM (from 100:0 to 100:50) with one drop of NEt_3 to give as a colorless oil, which was recrystallized by EtOH to obtain compound **3** (424 mg, 0.63 mmol) as colorless crystals (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.68 (m, 4H), 7.85 (t, J = 7.8 Hz, 2H), 7.63 – 7.51 (m, 5H), 1.19 (s, 36H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.81 (s), 155.08 (s), 143.28 (s), 106.03 (s), 92.17 (s), 18.74 (s), 11.35 (s). HRMS m/z (ESI$^+$) cald for $C_{42}H_{55}N_4Si_2$ ([M+H]$^+$), 671.3887, found 671.3901.

Figure S3. ^{1}H-NMR spectrum of 2-phenyl-4,6-bis(6-((triisopropylsilyl)ethynyl)pyridin-2-yl)pyrimidine in $CDCl_3$

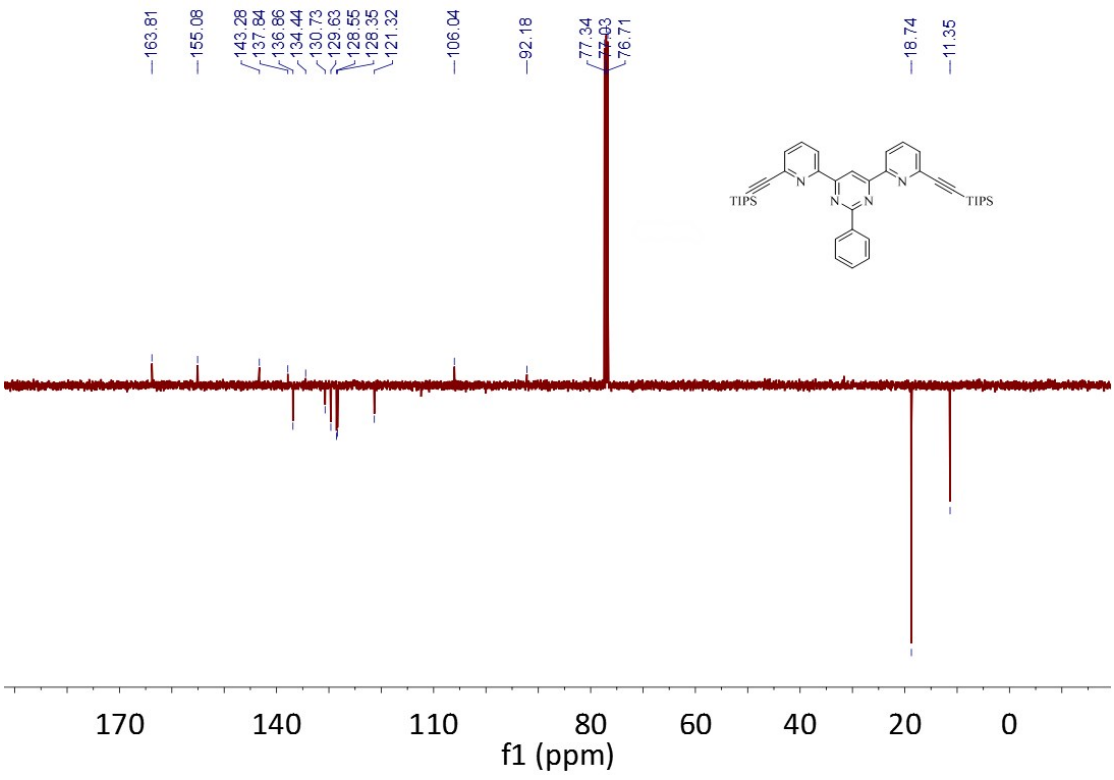


Figure S4. ^{13}C-NMR spectrum of 2-phenyl-4,6-bis(6-((triisopropylsilyl)ethynyl)pyridin-2-yl)pyrimidine in $CDCl_3$

Crystals of compound **3**, suitable for single-crystal X-ray diffraction analysis, were prepared by slow evaporation of a 10 mg mL^{-1} acetonitrile solution at room temperature. The crystals appeared as fine, colorless needles. A single crystal was mounted on a nylon loop using Paratone® oil.

Crystal Data for $C_{42}H_{54}N_4Si_2$ (M = 671.07 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 17.6814(2) Å, b =18.1633(2) Å, c = 12.39478(16) Å, β = 95.6934(12)°, V = 3960.98(8) $Å^3$, Z = 4, T = 100 K, μ(Cu Kα) = 1.055 mm^{-1}, $Dcalc$ = 1.125 g/cm^3, 37060 reflections measured (6.994° ≤ 2Θ ≤ 150.482°), 8026 unique (R_{int} = 0.0586, R_{sigma} = 0.0335) which were used in all calculations. The final R_1 was 0.0560 (I > 2σ(I)) and wR_2 was 0.1624 (all data).

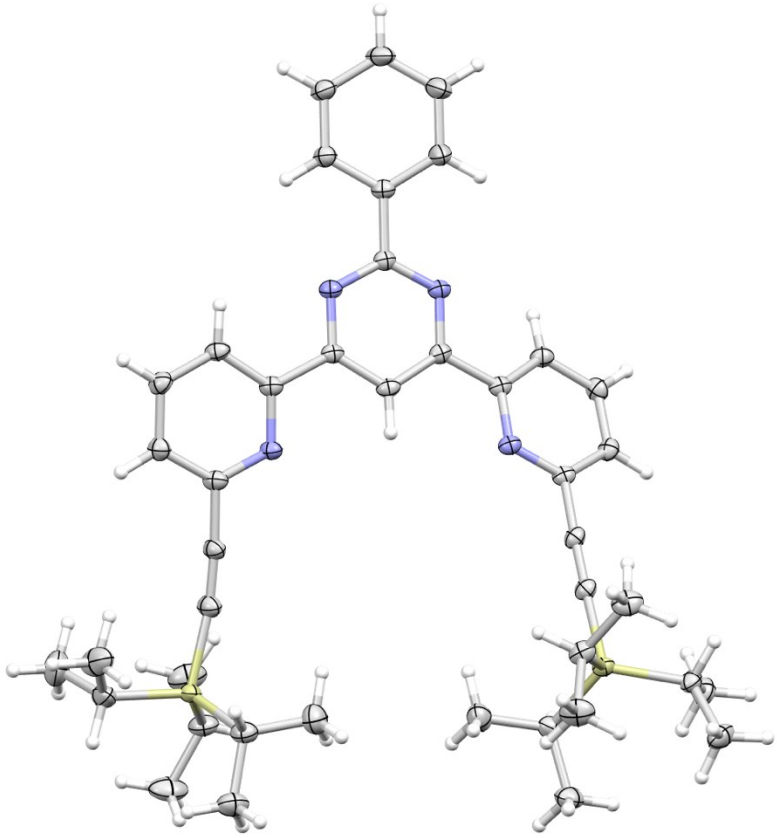
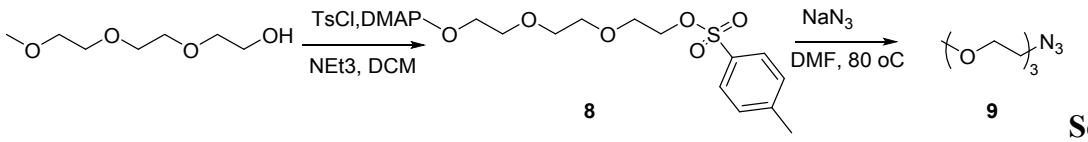


Figure S5. Asymmetric unit of the crystal structure of 2-phenyl-4,6-bis(6-((triisopropylsilyl)ethynyl)pyridin-2-yl)pyrimidine (**3**). Thermal displacement ellipsoids are drawn at the 50% probability level.



Scheme S1. Synthetic strategy for the azido-triethylene glycol.

2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (8)

Triethylene glycol monomethyl ether (9.7 mL, 61 mmol), NEt_3 (21.2 mL, 0,1525 mol) and 4-dimethylaminopyridine (DMAP; 1.74 g, 14.2 mmol) were dissolved in DCM (400 mL). The mixture was cooled to 0°C and 4-toluenesulfonylchloride (13.2 g, 69 mmol) was added. After several minutes, the solution got an orange color and the ice bath was removed. The mixture was stirred overnight at room temperature. The solution was washed with water and dried over $MgSO_4$. After evaporation of the solvent, column chromatography was used to purify the compound with silica as stationary phase and ethyl acetate/DCM 3/7 as the eluent. 2-(2-(2-methoxyethoxy)ethoxy)ethyl tosylate was obtained as a yellow oil (13.45 g, 42.3 mmol, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J=8.3 Hz, 2H, RO3S-C-*CH*=CH-), 7.33 (m, J=8.0, 2H, RO3S-C-CH=*CH*-), 4.41 (m,2H, Tos-*CH2*-), 3.65 (m, 2H, Tos-CH2-*CH2*-O-), 3.56 (m, 6H, *CH3*- O-CH2-CH2-O-CH2-) 3.51 (m, 2H), 3.34 (s, 3H, *CH3*-O-CH2-), 2.41 (s, 3H, RO3S-C-CH=CHC-*CH3*). The spectral data was identical to those reported in literature.[1]

2-(2-(2-Methoxyethoxy)ethoxy)ethyl azide (9)

8 (1 g, 3.15 mmol) and solidum azide (614.41 mg, 9.45 mmol) were dissolved in 10 mL of dry DMF in a 100 mL round-bottom flask under argon. The reaction mixture was placed in a preheated oil bath at 80 °C and stirred overnight. After cooling to room temperature, the reaction mixture was extracted by mixing EtOAc with water. The organic layer was collected and evaporated. The residue was dried in vacuum oven overnight to give the compound 12 as a colorless oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 – 3.64 (m, 8H), 3.56 (m, 2H), 3.42 – 3.35 (m, 5H). The spectral data was identical to those reported in literature.[1]

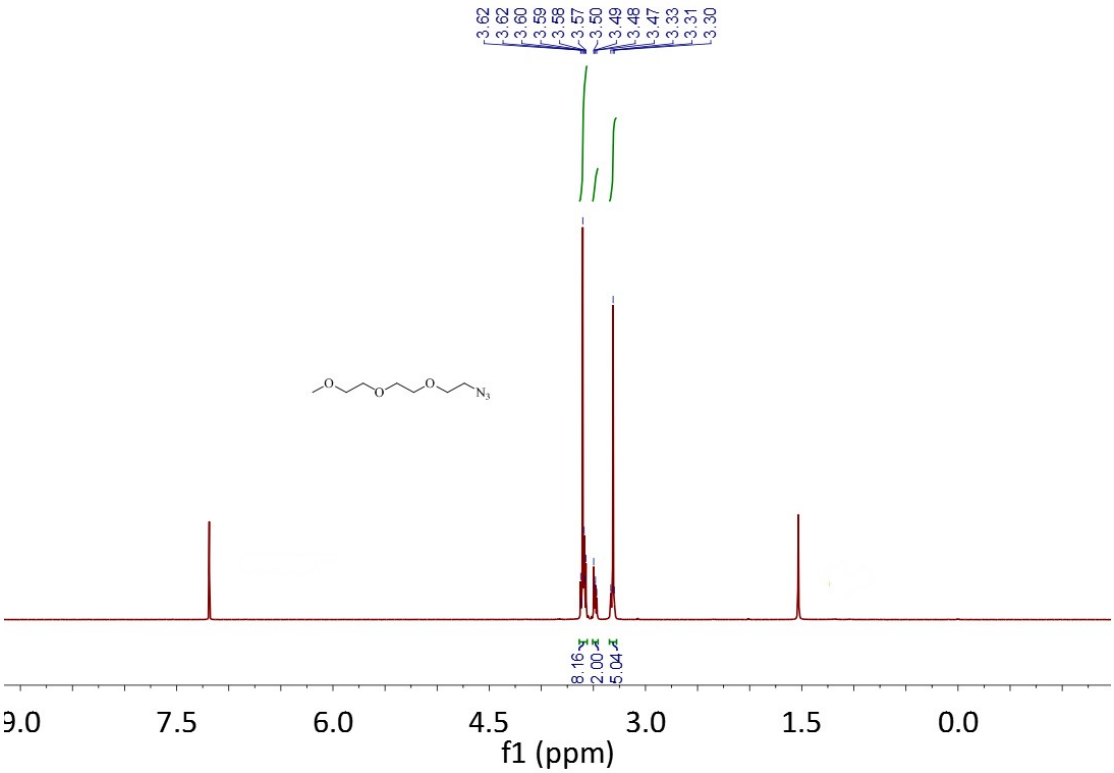


Figure S6. ^{1}H-NMR spectrum of 2-(2-(2-methoxyethoxy)ethoxy)ethyl azide in $CDCl_3$.

Synthesis of phenyl azide

To a solution of aniline (10 mmol) in 80 mL HCl (17 %) solution at room temperature was added ethanol until a clear solution was obtained. The reaction mixture was cooled down to 0 °C and $NaNO_2$ (1.5 eq.) was added quickly under argon atmosphere and

stirred for 30 min. NaN_3 (1.5 eq.) was slowly added and the mixture was stirred for additional 2 h at ambient temperature. The reaction mixture was extracted with diethyl ether (3 x 80 mL) and the combined organic fractions were washed with saturated $NaHCO_3$-solution (3 x 50 mL) and with brine (50 mL). After drying over $MgSO_4$ the ether was removed under reduced pressure and the phenyl azide was obtained without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.10 – 7.04 (m, 1H), 7.00 – 6.91 (m, 2H). The spectral data was identical to those reported in literature.[7]

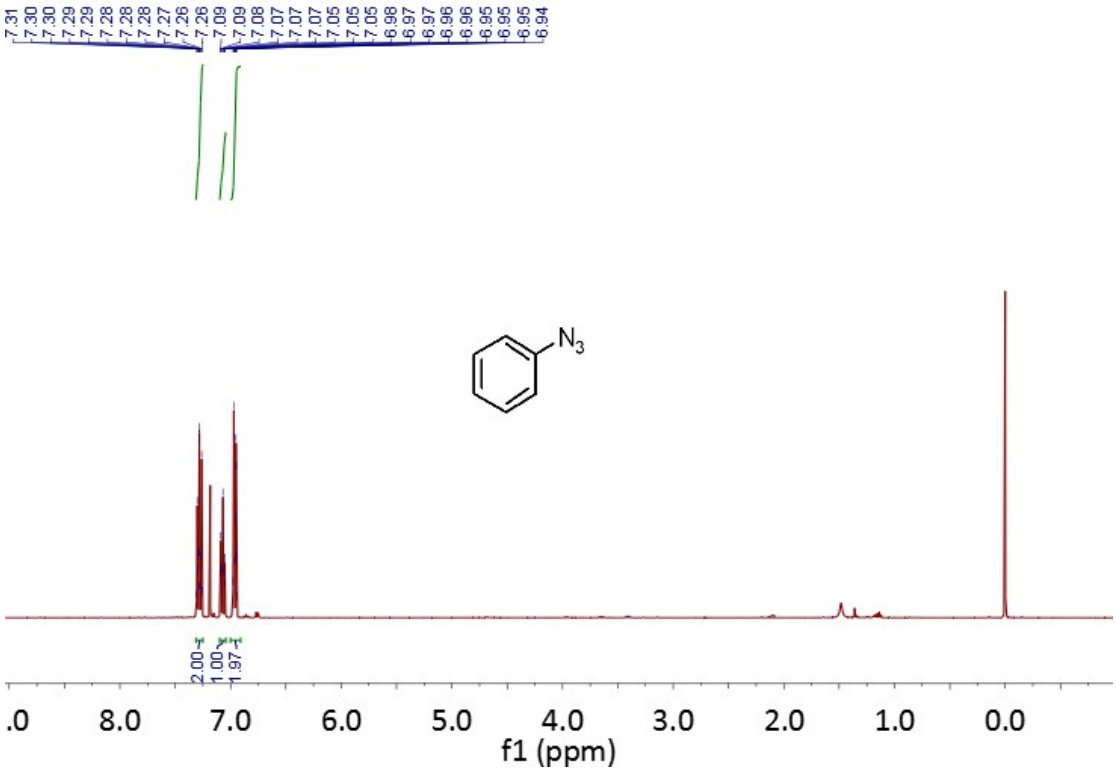
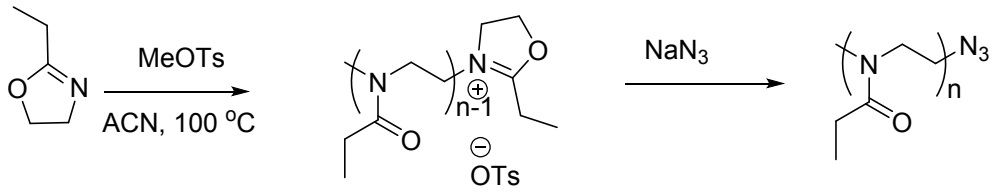


Figure S7. ^{1}H-NMR spectrum of phenyl azide in $CDCl_3$.

Polymer synthesis

Synthesis of azido end-functionalized PEtOx



Scheme S2. Synthesis of poly(2-ethyl-2-oxazoline) azido end-functionalized polymers. PEtOx polymers having different degree of polymerization were synthesized by cationic ring opening polymerization. A typical example is given below for the PEtOx having a DP of 20.

EtOx (1.211 mL, 12 mmol) and MeOTs (0.091 mL, 0.652 mmol) were dissolved in 1.8 mL of acetonitrile in a round-bottom flask in a glovebox, and the mixture was stirred at 100 °C for the appropriate time, then to end-cap the reaction NaN_3 was added and stirred for 12 h. The mixture was taken out of the glovebox and the solvent was evaporated. Water was added and solution was purified by a PD-10 desalting column to give the product (40%). $PEtOx_{20}$-N_3 (10), ^1H NMR, 300 MHz, $CDCl_3$: 0.96-1.20 (3H, O=C-CH_2-CH_3); 2.25-2.50 (2H, O=C-CH_2-CH_3); 3.43 (4H, N-CH_2-CH_2). SEC-RI (PMMA calibration), M_n = 3100 and Đ = 1.12.

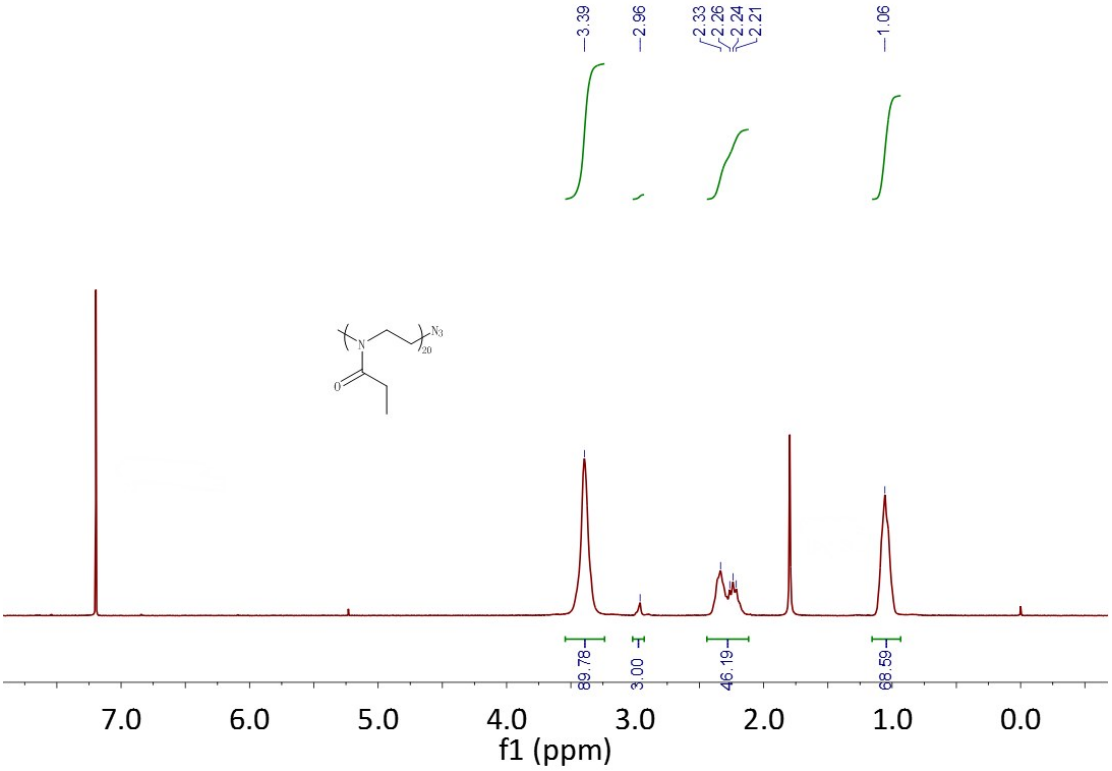


Figure S8. ^{1}H-NMR spectrum of PEtOx$_{20}$-N$_3$ in $CDCl_3$.

Synthesis of PEtOx$_{50}$-N$_3$ (11) was performed under the similar conditions. ^{1}H NMR, 300 MHz, $CDCl_3$: 0.96-1.20 (3H, O=C-CH$_2$-*CH$_3$*); 2.25-2.50 (2H, O=C-*CH$_2$*-CH$_3$); 3.43 (4H, N-*CH$_2$*-*CH$_2$*). SEC-RI (PMMA calibration), M_n = 8800 and Đ = 1.16.

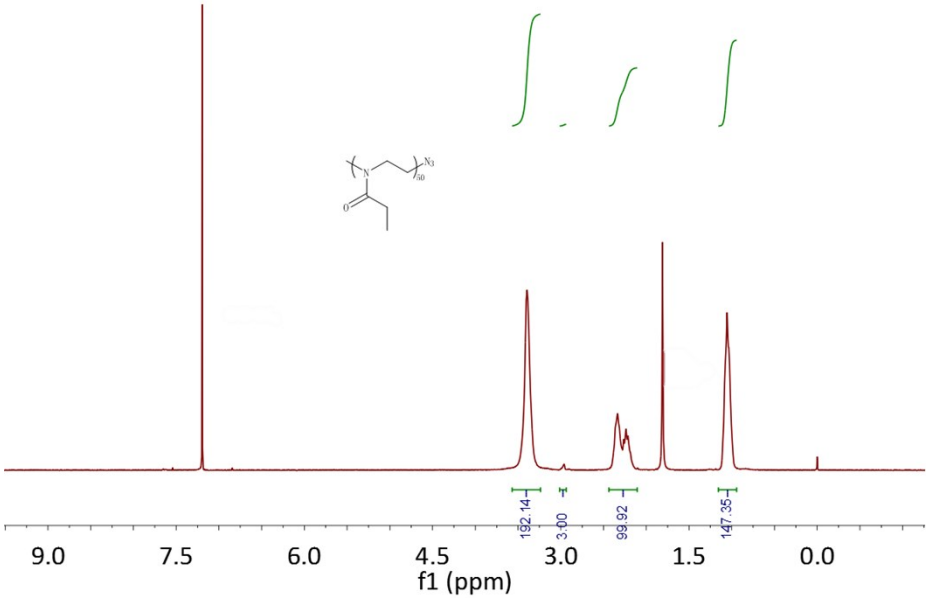


Figure S9. ^{1}H-NMR spectrum of PEtOx$_{50}$-N$_3$ in $CDCl_3$.

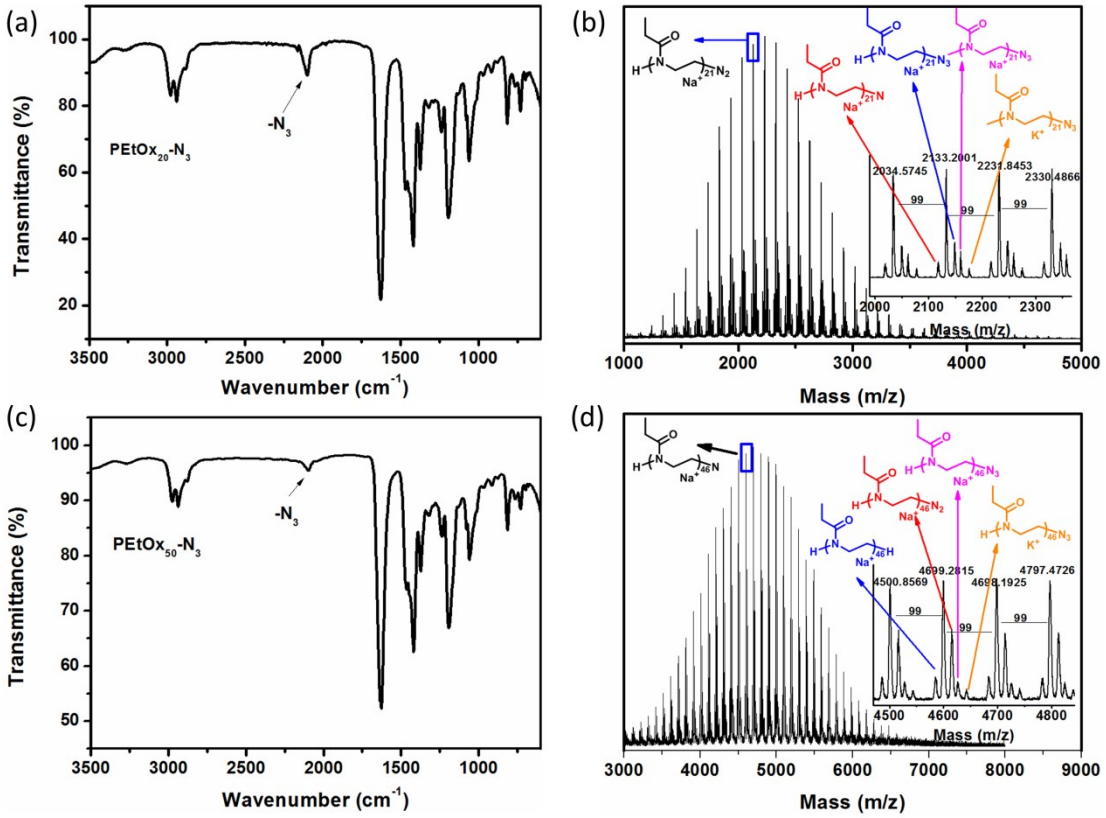


Figure S10. (a) FT-IR spectrum of $PEtOx_{20}$-N_3, (b) MALDI-TOF mass spectrum of $PEtOx_{20}$-N_3, (c) FT-IR spectrum of $PEtOx_{50}$-N_3, (d) MALDI-TOF mass spectrum of $PEtOx_{50}$-N_3.

Synthesis of azido end-functionalized PEG

The general procedure employed for the preparation of azido end-functionalized PEG was as follows: PEG_7 monomethyl ether (20 mmol, 1 equiv) was initially dried via azeotropic distillation with toluene (3 x 100 mL). Subsequently, NEt_3 (24 mmol, 1.2 equiv) and dichloromethane (80 mL) were added and the mixture was cooled to 0 °C before methanesulfonyl chloride (30 mmol, 1.5 equiv) was added dropwise. The reaction was kept at 0 °C for 30 min and then at room temperature for 12 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was dissolved in DMF (50 mL), and NaN_3 (200 mmol, 10 equiv) was added. The reaction mixture was heated to 65 °C for 12 h, cooled to room temperature and concentrated in

vacuo. The residue was dissolved in water (200 mL) and then washed with dichloromethane (100 mL × 2). The organic extracts were collected, washed with water (200 mL) and saturated NaCl (200 mL × 2), dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the desired monoazido PEG (PEG_{17}-N_3). ^1H NMR (400 MHz, $CDCl_3$): δ H 3.37-3.41 (s, 3H, O*CH*$_3$ end group, and t, 2H, C*H*$_2$$N_3$ end group), 3.45-3.85 (m, C*H*$_2$O) ppm. The spectral data was identical to those reported in literature.[8]

Synthesis of PEG_{45}-N_3 (13) was performed under the similar conditions. SEC-RI (PMMA calibration), Mn = 3900 g/mol and Đ = 1.05.

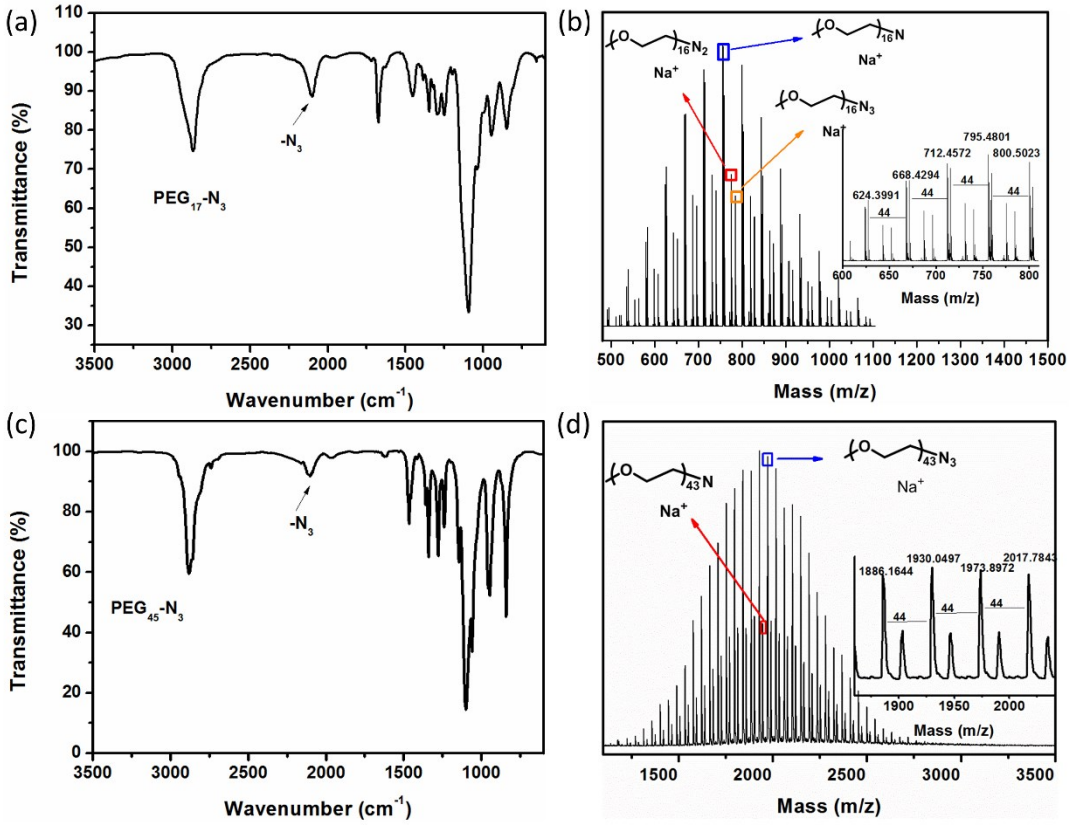


Figure S11. (a) FT-IR spectrum of PEG_{17}-N_3, (b) MALDI-TOF mass spectrum of PEG_{17}-N_3, (c) FT-IR spectrum of PEG_{45}-N_3, (d) MALDI-TOF mass spectrum of PEG_{45}-N_3.

Click reaction general procedure A:

4,6-Bis(6-(1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1H-1,2,3-triazol-4-yl)pyridin-2-yl)-2-phenylpyrimidine (L1)

3 (100 mg, 0.15 mmol) was suspended in a degassed THF/water mixture (5:1, 10 mL) and treated with a 5-fold excess of tetra-*n*-butyl ammonium fluoride (TBAF; 235.31 mg, 0.9 mmol) under argon and stirred for 1 h. To this was added 2-(2-(2-methoxyethoxy)ethoxy)ethyl azide **9** (70.5 mg, 0.375 mmol), $CuSO_4$ (52.65 mg, 0.33 mmol), and sodium ascorbate (70 mg, 0.345 mmol in 0.7 mL THF) and the mixture was stirred for 48 h at room temperature under argon. The solvents were evaporated and the residue was purified by column chromatography on silica with pentane/acetone (5:1 to 1:1) to give compound **4** (66.33 mg, 0.09 mmol) as yellowish oil (60 %). Note that for the macroligand (L3 – L6) synthesis, a copper removal procedure was applied by dissolving the macroligand in dichloromethane and then washing with 5% EDTA aqueous solution. The organic phase was collected and the solvent was removed by reduced pressure to obtain the pure macroligand. ^{1}H NMR (300 MHz, CD_3CN) δ 9.42 (s, 1H), 8.89 – 8.62 (m, 4H), 8.55 (s, 2H), 8.34 (d, J = 6.9 Hz, 2H), 8.03 (t, J = 6.8 Hz, 2H), 7.57 (s, 3H), 4.75 (s, 4H), 3.98 (s, 4H), 3.65 – 3.55 (m, 4H), 3.48 (m, 4H), 3.40 (m, 4H), 3.28 (m, 4H), 3.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.97, 164.19, 154.20, 150.24, 148.18, 71.76, 70.75, 70.44, 69.74, 50.53. HRMS m/z (ESI^+) cald for $C_{38}H_{45}N_{10}O_6$ ($[M+H]^+$), 737.3445, found 737.3449.

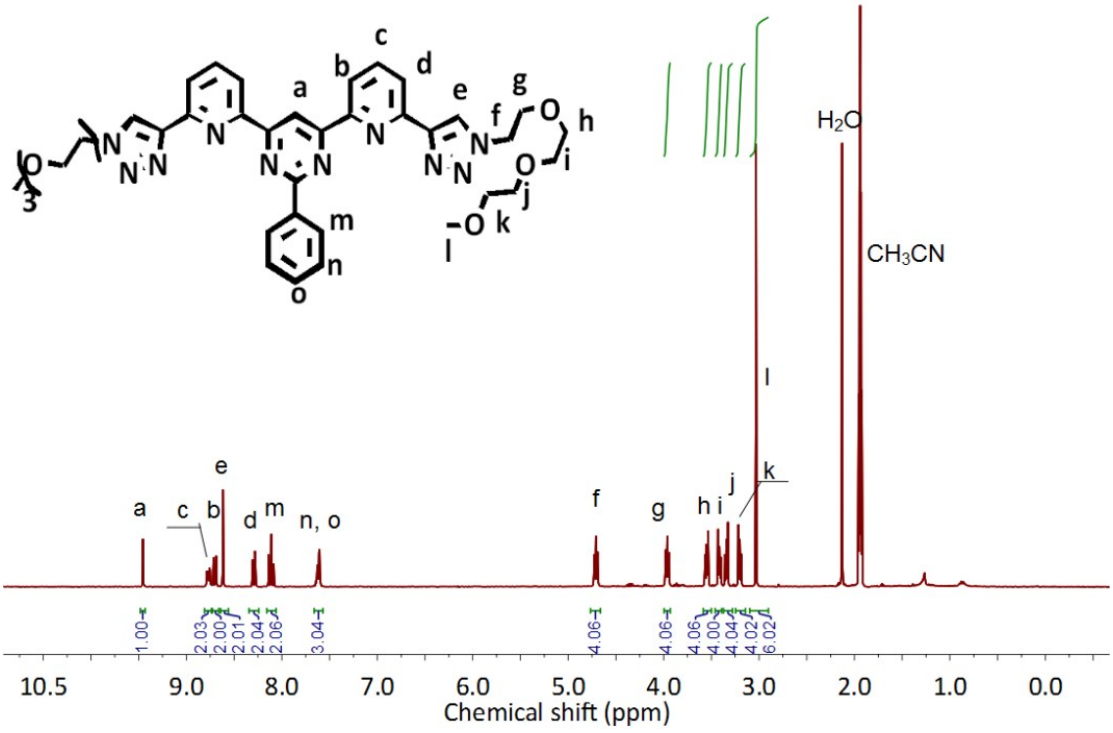


Figure S12. ^{1}H-NMR spectrum of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate in CD_3CN.

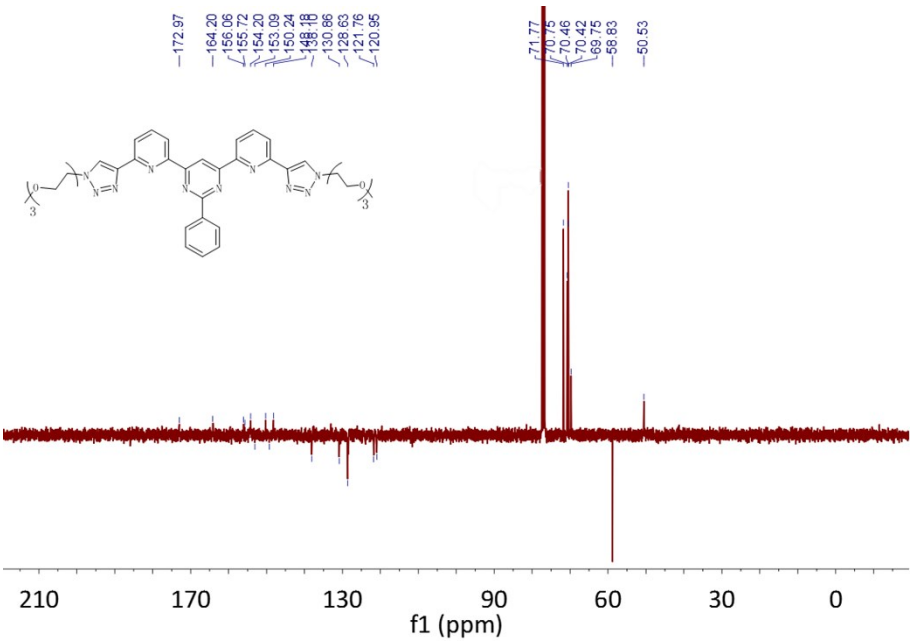


Figure S13. ^{13}C-NMR spectrum of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate in $CDCl_3$.

The above procedure was also used for the synthesis of the organic and macromolecular ligands L2, L3, L4, L5, and L6.

L2 was obtained as a yellow solid in a yield of 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.80 (s, 2H), 8.72 – 8.68 (m, 2H), 8.65 (d, J = 6.9 Hz, 2H), 8.36 (d, J = 7.8 Hz, 2H), 8.03 (t, J = 7.9 Hz, 2H), 7.73 (dd, J = 6.8, 3.0 Hz, 4H), 7.52 (d, J = 7.7 Hz, 3H), 7.32 – 7.28 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.05, 154.63, 150.91, 149.77, 148.83, 147.81, 138.25, 137.73, 136.88, 130.92, 129.84, 128.92, 128.63, 128.45, 122.13, 121.62, 120.28, 111.91. HRMS m/z (ESI$^+$) cald for $C_{36}H_{25}N_{10}$ ([M+H]$^+$), 597.2264, found 597.2267.

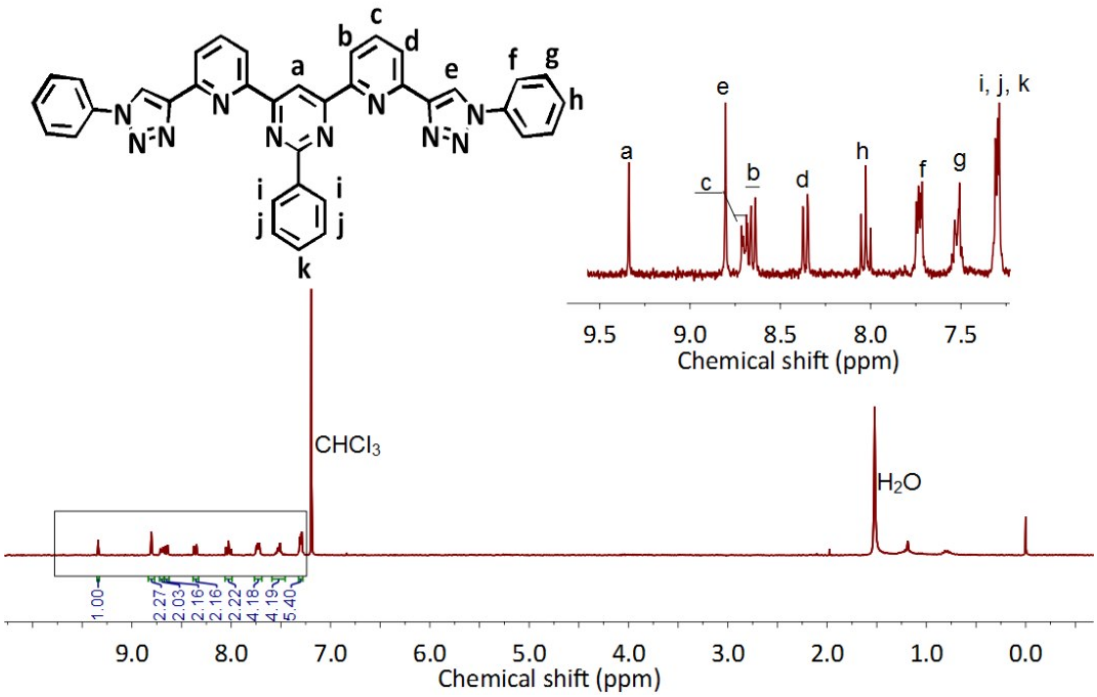


Figure S14. ^{1}H-NMR spectrum of **L2** in $CDCl_3$.

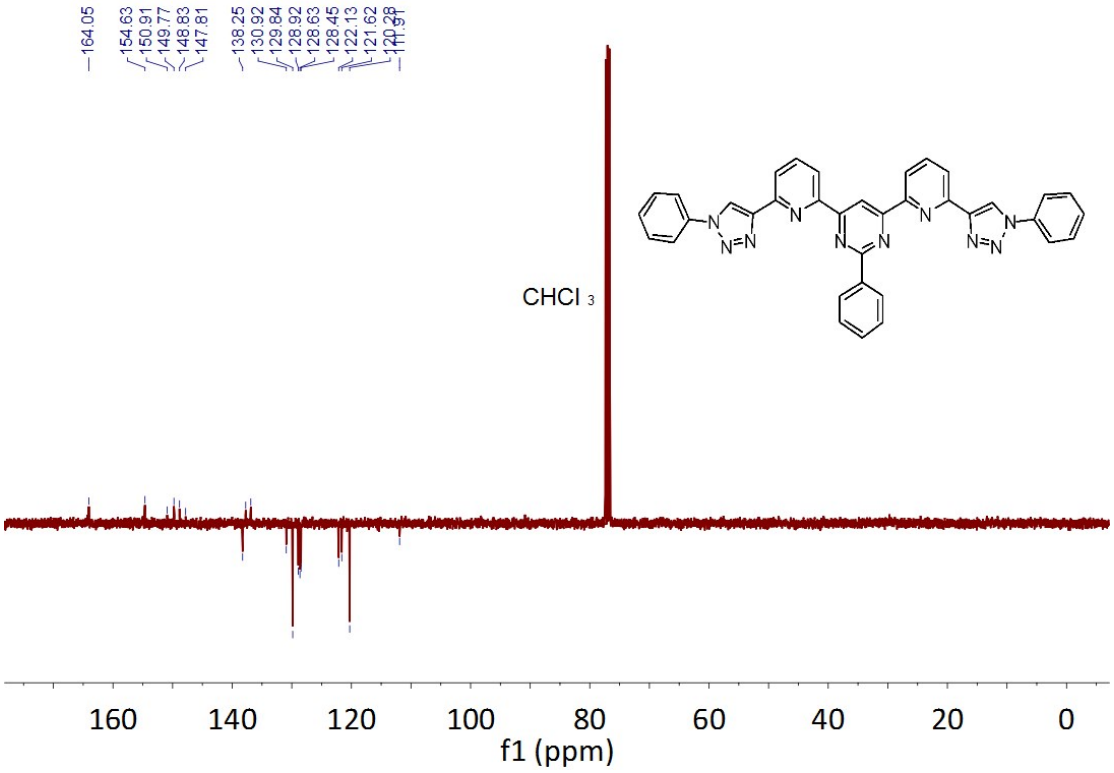


Figure S15. ^{13}C-NMR spectrum of **L2** in $CDCl_3$.

L3 was obtained as a white solid in a yield of 75%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.42 (s, 4H), 2.52 – 2.11 (m, 2H), 1.08 (s, 3H). SEC-RI (PMMA calibration), M_n = 8800 g/mol and Đ = 1.17.

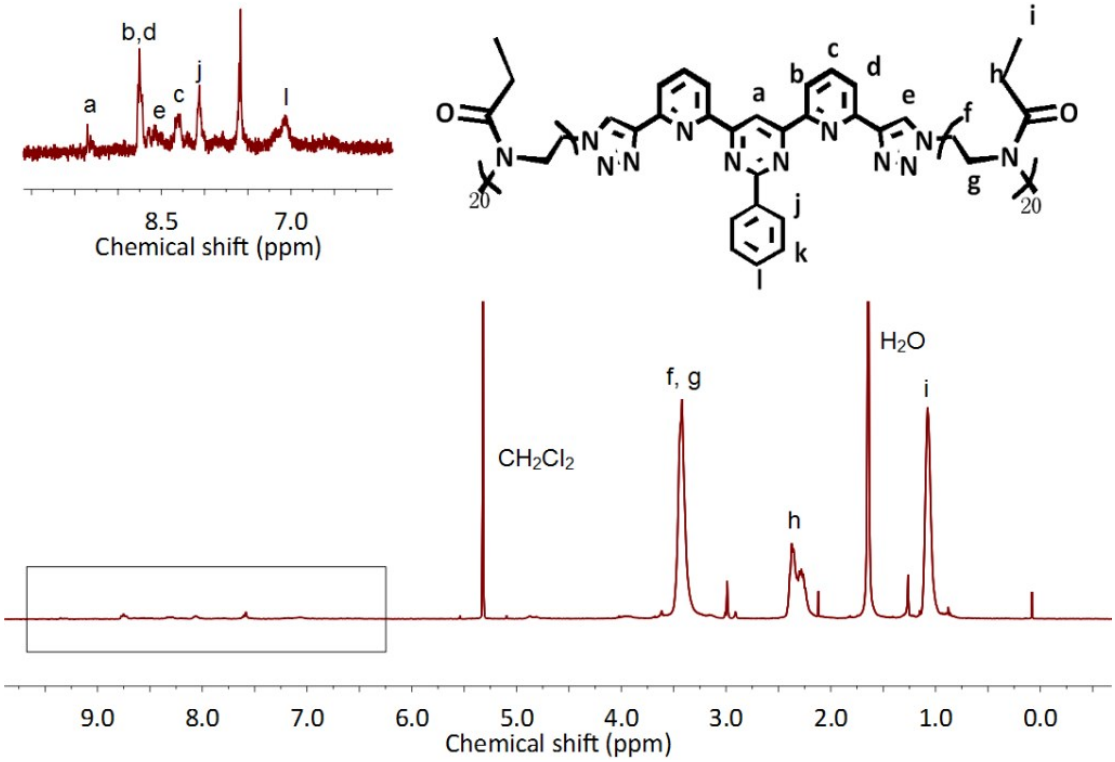


Figure S16. ^{1}H-NMR spectrum of **L3** in CD_2Cl_2.

L4 was obtained as a white solid in a yield of 74%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.44 (d, J = 9.2 Hz, 4H), 2.32 (ddd, J = 21.4, 13.7, 6.8 Hz, 2H), 1.08 (s, 3H). SEC-RI (PMMA calibration), M_n = 17000 g/mol and Đ = 1.08.

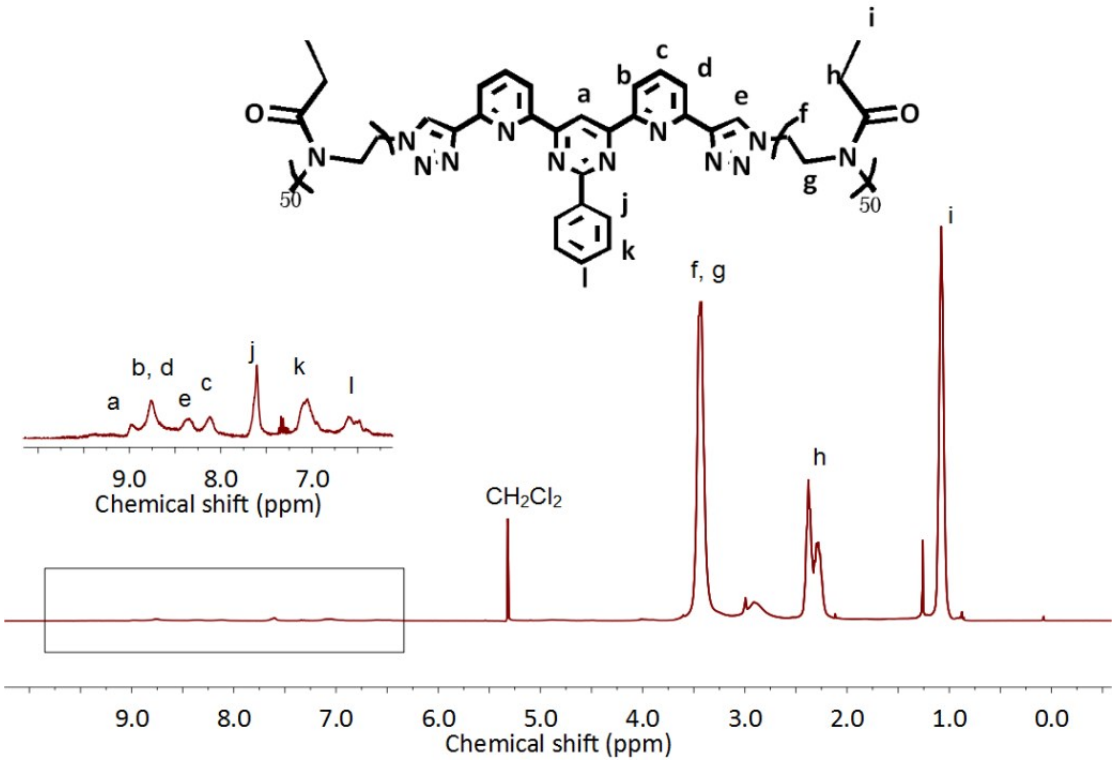


Figure S17. ^{1}H-NMR spectrum of **L4** in CD_2Cl_2.

L5 was obtained as yellowish oil in a yield of 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.76 (d, J = 7.9 Hz, 2H), 8.67 (d, J = 7.3 Hz, 2H), 8.55 (s, 2H), 8.33 (d, J = 7.0 Hz, 2H), 8.03 (t, J = 7.8 Hz, 2H), 7.57 (d, J = 7.3 Hz, 3H), 4.74 (t, J = 4.9 Hz, 4H), 3.97 (t, J = 5.0 Hz, 4H), 3.69 – 3.34 (m, 126H).

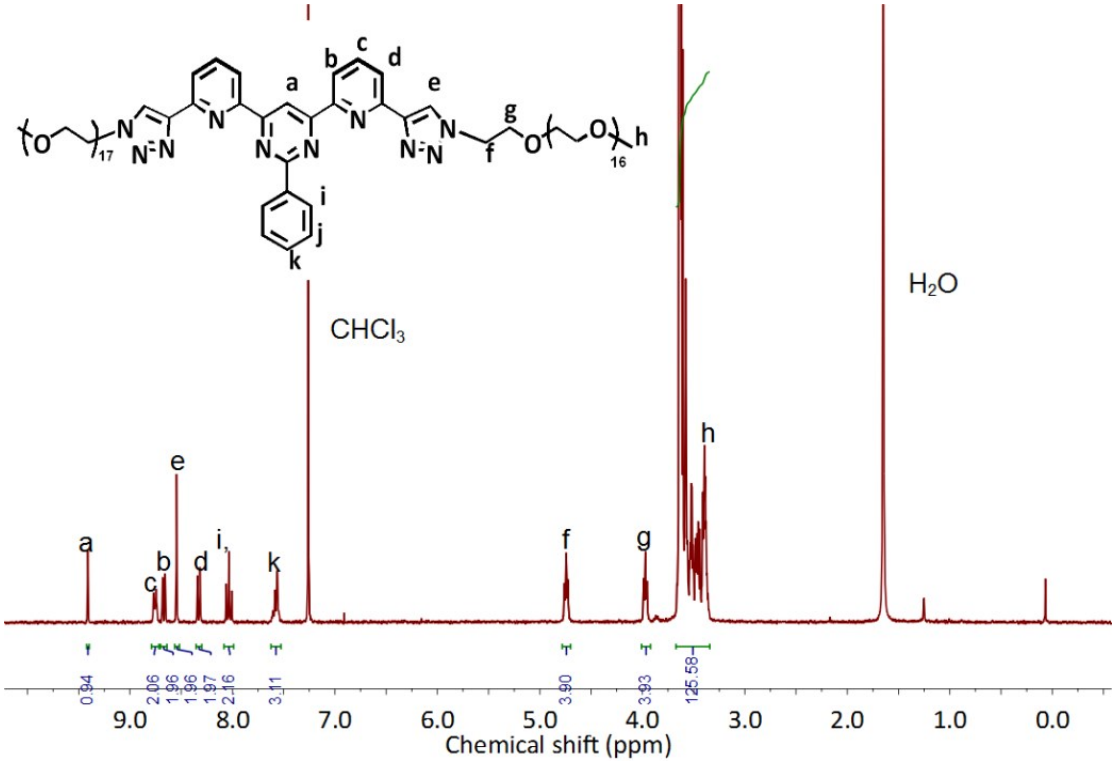


Figure S18. ^{1}H-NMR spectrum of **L5** in $CDCl_3$.

L6 was obtained as a white solid in a yield of 82%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.45 (s, 1H), 8.77 (dd, *J* = 7.7, 1.7 Hz, 2H), 8.72 – 8.66 (m, 2H), 8.56 (s, 2H), 8.36 – 8.27 (m, 2H), 8.06 (t, *J* = 7.8 Hz, 2H), 7.64 – 7.53 (m, 3H), 4.74 (t, *J* = 5.0 Hz, 4H), 3.98 (d, *J* = 5.1 Hz, 4H), 3.77 (dd, *J* = 5.6, 3.9 Hz, 2H), 3.66 – 3.31 (m, 372H). SEC-RI (PMMA calibration), M_n = 6500 g/mol and Đ = 1.08.

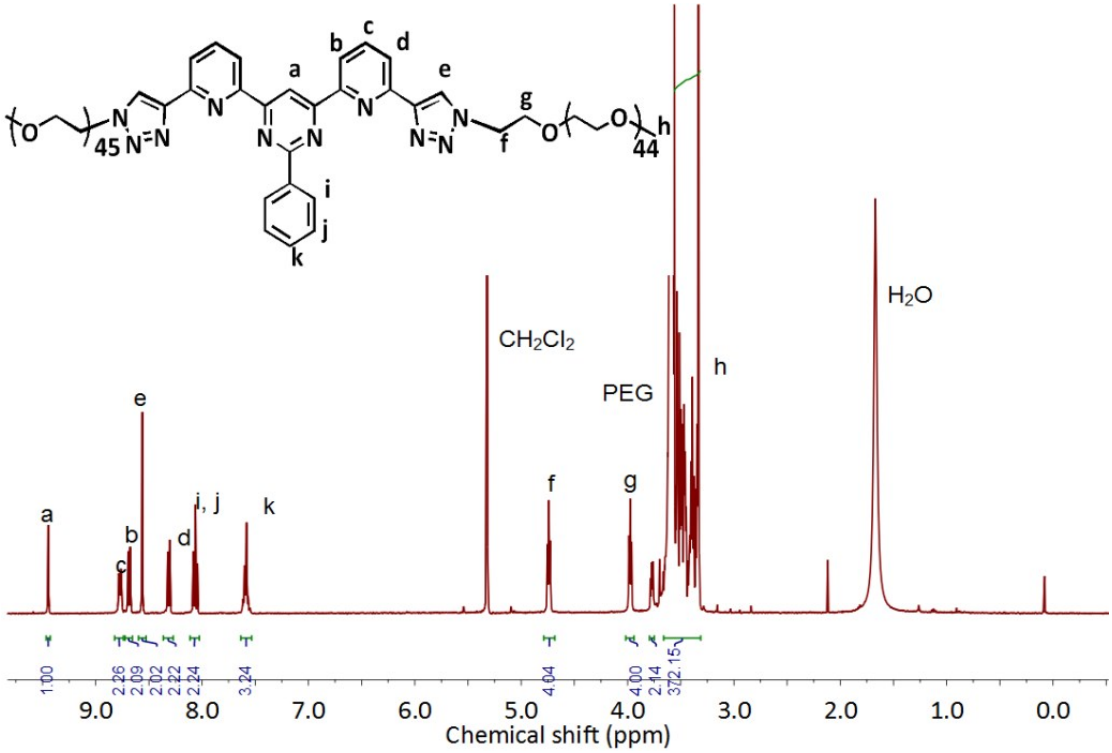


Figure S19. ^{1}H-NMR spectrum of **L6** in CD_2Cl_2.

S2. FT-IR, SEC and MALDI-TOF characterization of products

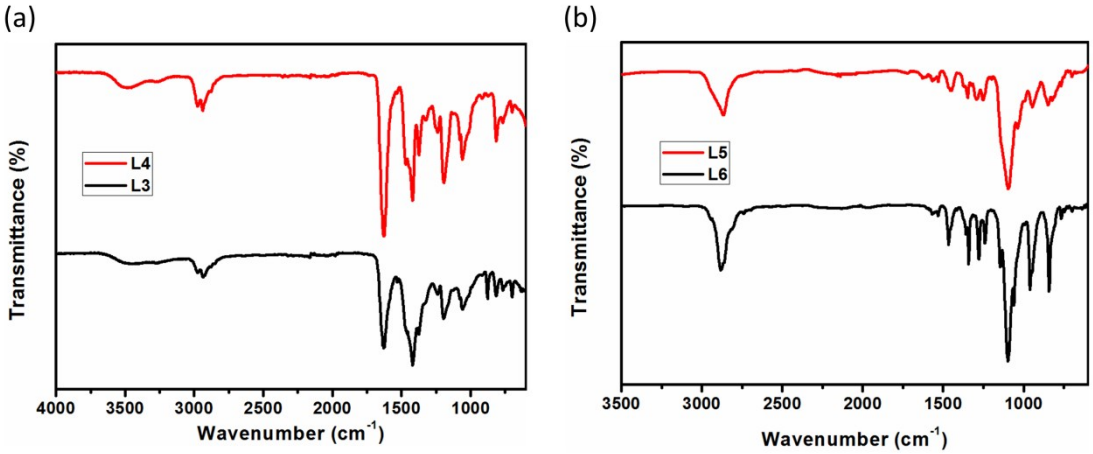


Figure S20. FT-IR spectra of: (a) **L3** and **L4**, (b) **L5** and **L6**.

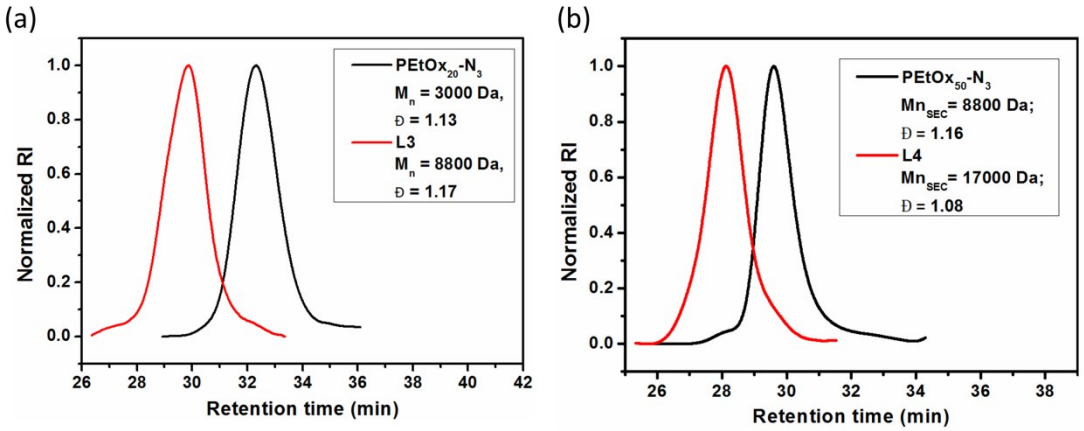


Figure S21. SEC traces of: (a) $PEtOx_{20}$-N_3 and **L3**, and (b) $PEtOx_{50}$-N_3 and **L4**.

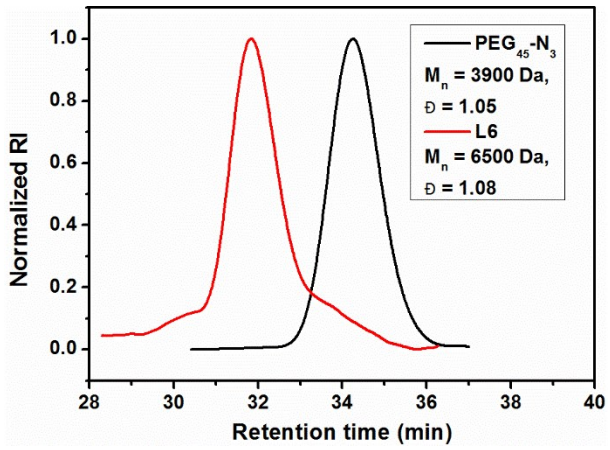


Figure S22. SEC-RI traces of PEG_{45}-N_3 and L6, respectively.

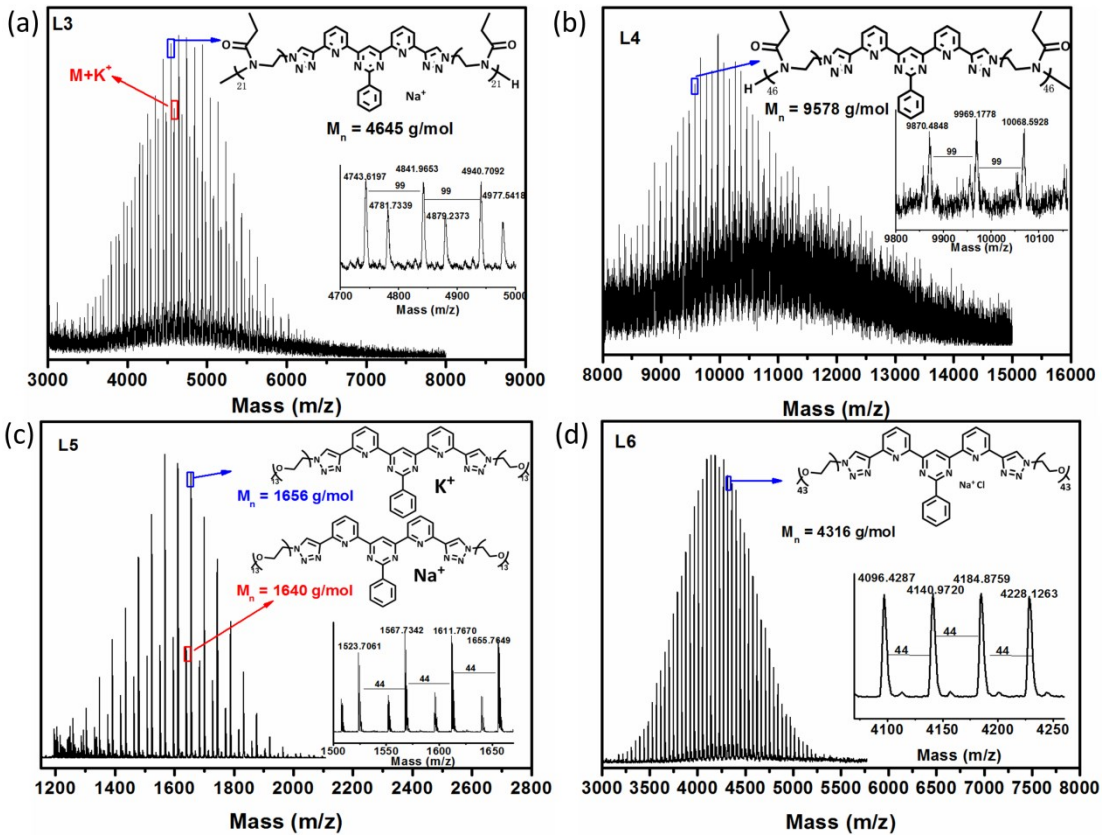


Figure S23. MALDI-TOF MS characterization of **L3**, **L4**, **L5**, and **L6**.

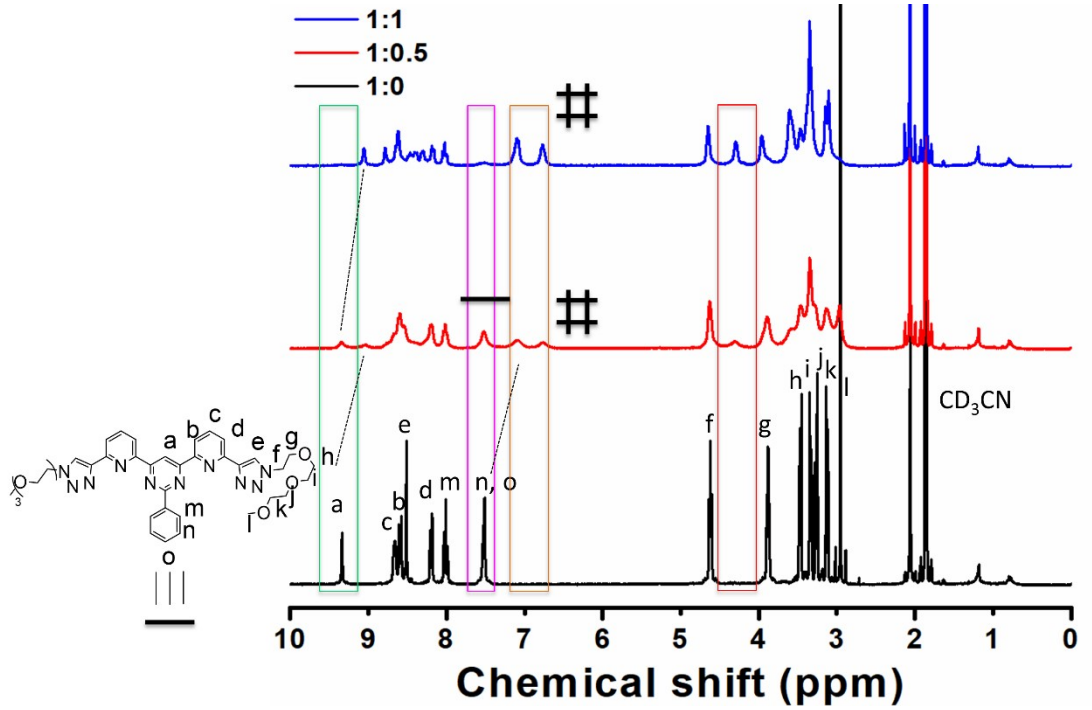


Figure S24. ^{1}H NMR titration involving **L1** with addition of $Zn(BF_4)_2$ (400 MHz, CD_3CN, 25 ˚C).

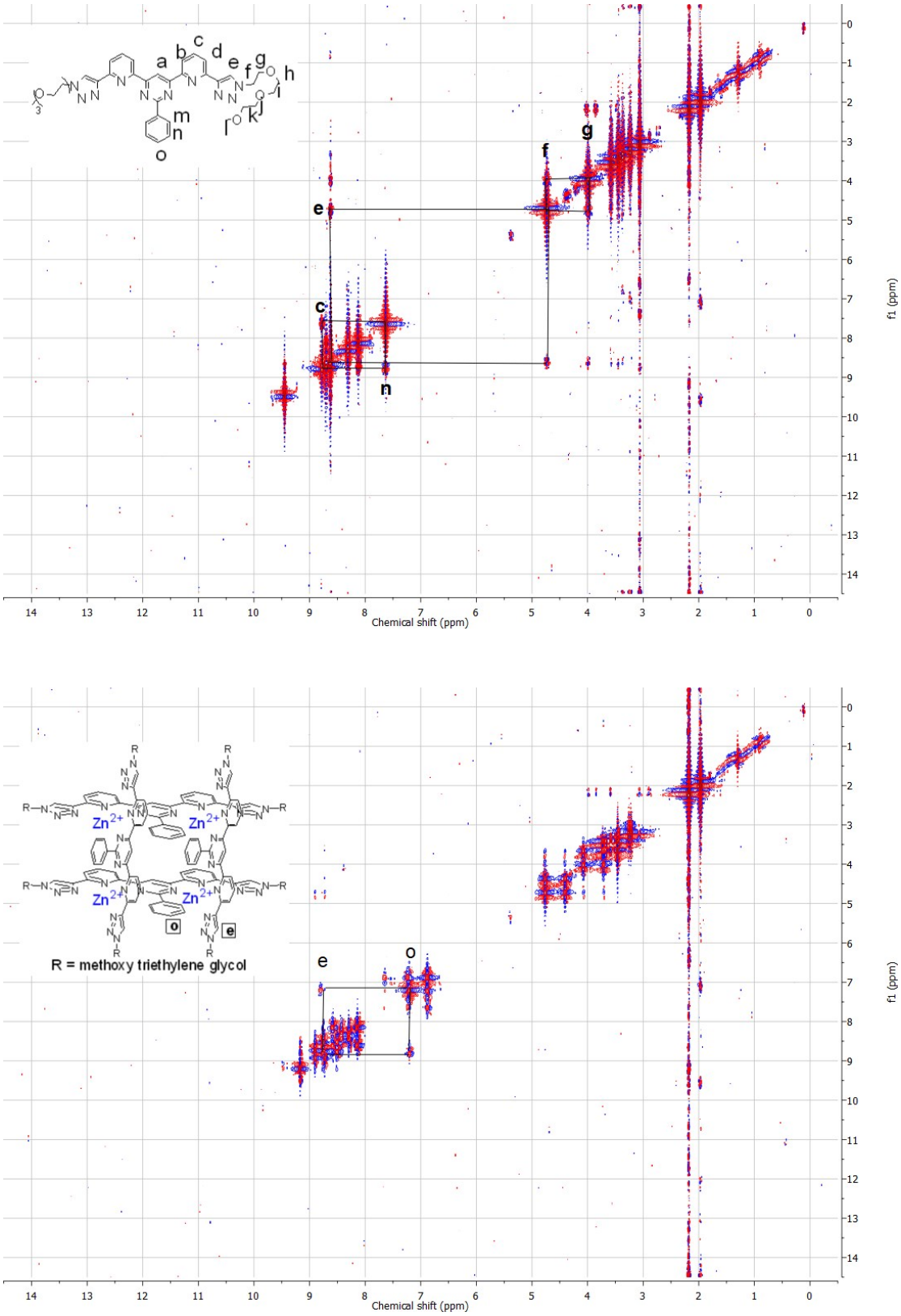


Figure S25. ^{1}H NOESY spectrum (400 MHz, 25 °C, CD_3CN) of L1 (top; note that there is no cross-peak between the peaks of protons o at 7.5 ppm and e at 8.5 ppm)) and Zn^{2+} complex **L1** (bottom; cross-peak present for signals o and e).

), respectively.

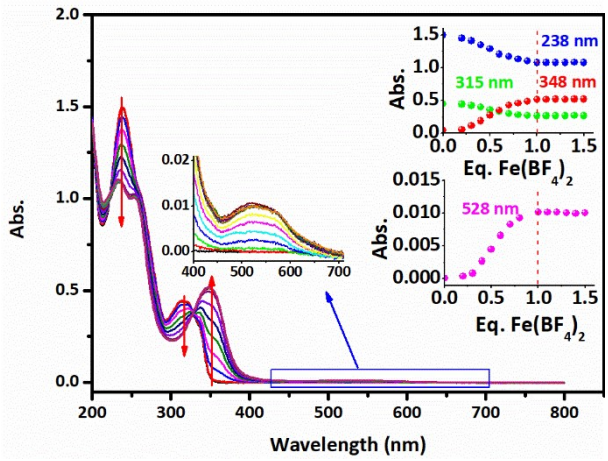


Figure S26. UV-vis spectroscopy titration experiments: (a) stepwise addition of 2.4 µL of 1.4 x 10^{-3} mol/L of solution of $Fe(BF_4)_2$ to a 2.3 x 10^{-5} mol/L of **L1** in CH_3CN,

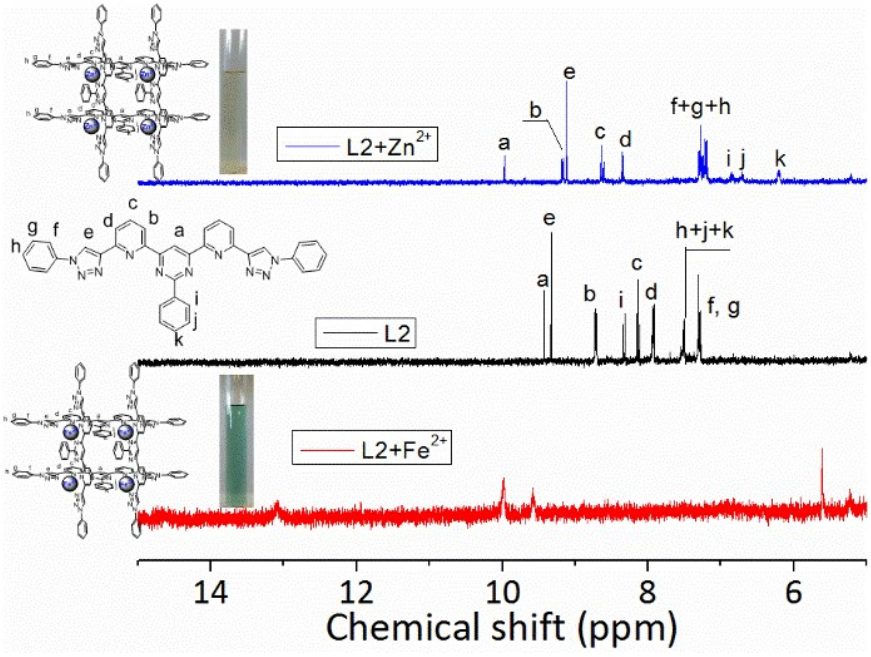


Figure S27. ^1H NMR spectrum of **L2** (middle, CD_3CN), and its corresponding Fe^{2+} complex (bottom, CD_3CN), as well as Zn^{2+} complex (top, CD_3CN).

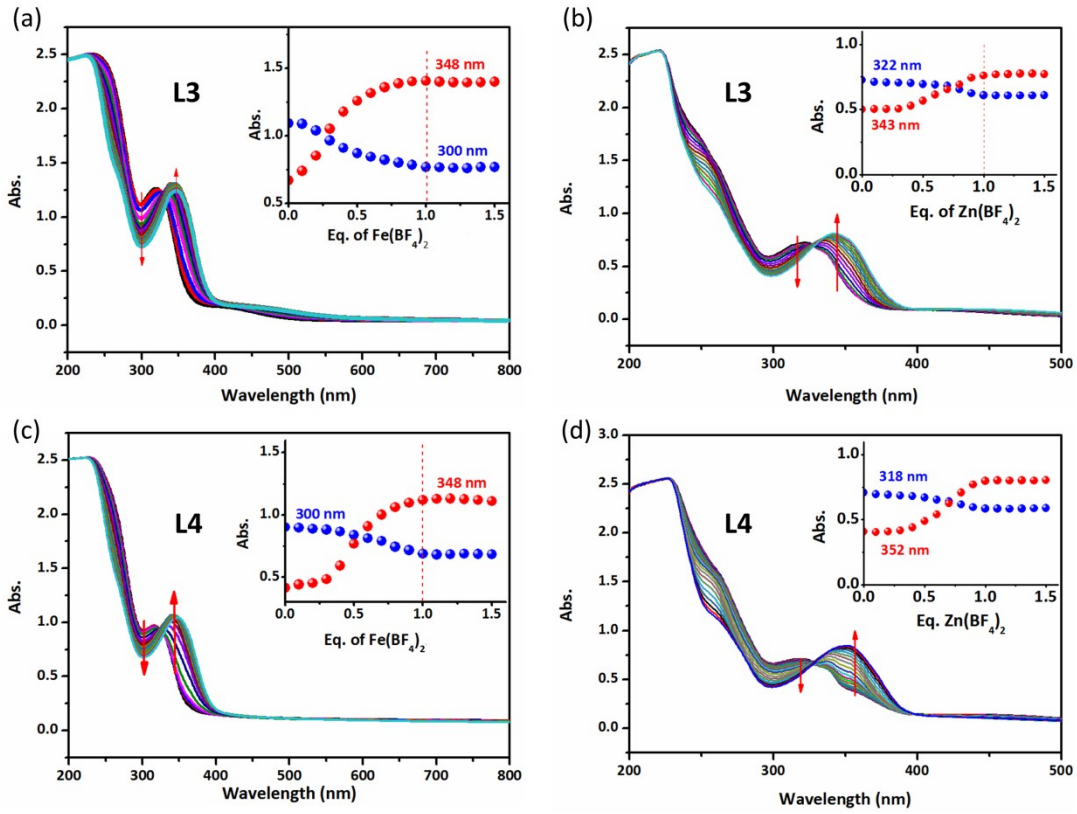


Figure S28. UV-vis spectroscopy titration experiments: (a) stepwise addition of 4.8 µL of 1.3 x 10^{-3} mol/L of solution of $Fe(BF_4)_2$ to a 4.17 x 10^{-5} mol/L of **L3** in CH_3CN, (b) stepwise addition of 3.4 µL of 1.8 x 10^{-3} mol/L of solution of $Zn(BF_4)_2$ to a 4.17 x 10^{-5} mol/L of **L3** in CH_3CN, (c) stepwise addition of 4.8 µL of 1.3 x 10^{-3} mol/L of solution of $Fe(BF_4)_2$ to a 4.17 x 10^{-5} mol/L of **L4** in CH_3CN, and (d) stepwise addition of 3.4 µL of 1.8 x 10^{-3} mol/L of solution of $Zn(BF_4)_2$ to a 4.17 x 10^{-5} mol/L of **L4** in CH_3CN. The inset graphs show the changes in the absorption with the increase of the amount of transition metal ions.

S3. References

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