Supporting information for

Conformational control in a bipyridine linked π-conjugated oligomer: Cation mediated helix defolding and refolding

Kizhumuri P. Divya,[a] Sivaramapanicker Sreejith,[a] Cherumuttathu H. Suresh[b] and Ayyappanpillai Ajayaghosh*[a]

* To whom correspondence should be addressed at:

Photosciences and Photonics Group,

Chemical Sciences and Technology Division,

National Institute for Interdisciplinary Science and Technology (NIIST),

CSIR, Trivandrum-695019, India

Tel: +91-471-2515306 Fax: +91-471-2490186, 2491712

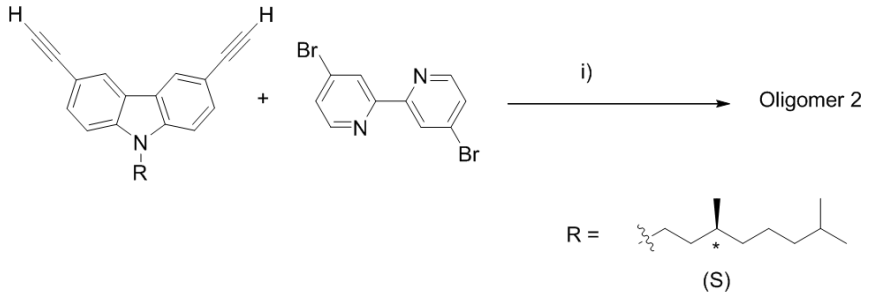
Email: ajayaghosh62@gmail.com

1. Experimental section

General

Solvents and reagents were purified and dried by usual methods. All starting materials were obtained from commercial suppliers and used as received. All melting points were determined with Mel-Temp-II melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR were measured on a 300 MHz Bruker Avance DPX Spectrometer. FT-IR spectrum was obtained on a Nicolet Impact 400D infrared spectrometer. High Resolution Mass Spectra were recorded with a JEOL JMS600. MALDI-TOF mass spectrometry was conducted on a Axima-CFR+ Kratos analytical Shimadzu mass spectrometer using 2,5-dihydrobenzoic acid as the matrix. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were measured on a SPEX-Fluorolog F112X spectrofluorimeter. CD spectra were recorded on JASCO-J-810 spectropolarimeter equipped with a JASCO PTC-423S Peltier type temperature control system. The gel permeation chromatography was performed on a Waters GPC system with Waters 510 pump and Waters 2487 UV-vis detector, using polystyrene as standards and THF as eluent. The flow rate of THF was maintained as 1 mL/min. All the Photophysical experiments were done with optically transparent solution.

2. Synthesis and characterization.



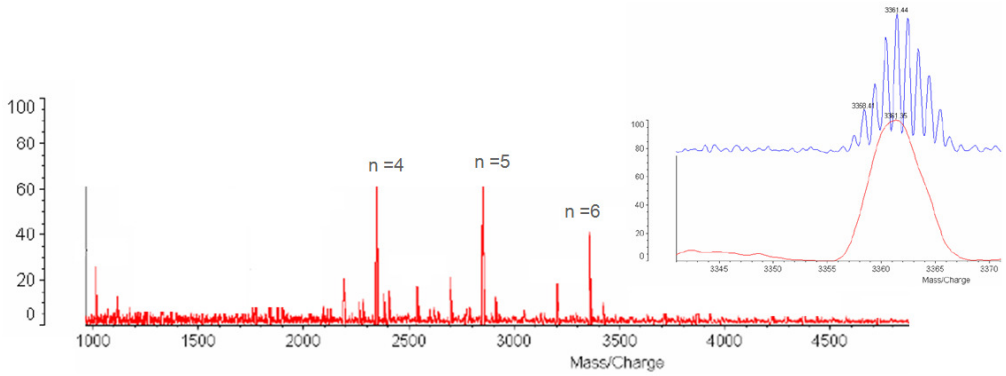
Scheme 1: Synthesis of oligomer **2**. Reagents and conditions; i) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, 64 °C.

2a) General procedure for the synthesis of oligomer 2

(*S*)-9-(3,7-dimethyloctyl)-3,6-diethynyl-9H-carbazole was reacted with one equivalent of the 4,4'-dibromo-2,2'-bipyridine using the standard Sonogashira coupling procedure under reflux condition. After 24 h, the reaction mixture was concentrated and the residue obtained was stirred with methanol for 2 h. The precipitate formed was filtered and redissolved in chloroform. The organic layer was washed with saturated aq. EDTA solution. The product obtained was concentrated by partial removal of the solvent and reprecipitated with methanol followed by repeated precipitation from methanol and hexane. The product thus obtained was filtered through a short alumina column using $CHCl_3$-hexane mixture as the eluent to get the oligomers as brownish yellow solids. The molecular weights were determined by GPC analyses. In order to check the purity, the samples were again reprecipitated from chloroform using methanol followed by repeated washing with methanol and hexane. Repetition of GPC showed no change in the molecular weight. The purity of the oligomers was also confirmed by recording the emission spectra after repeated washing with solvents. In all cases the emission spectra were the same.

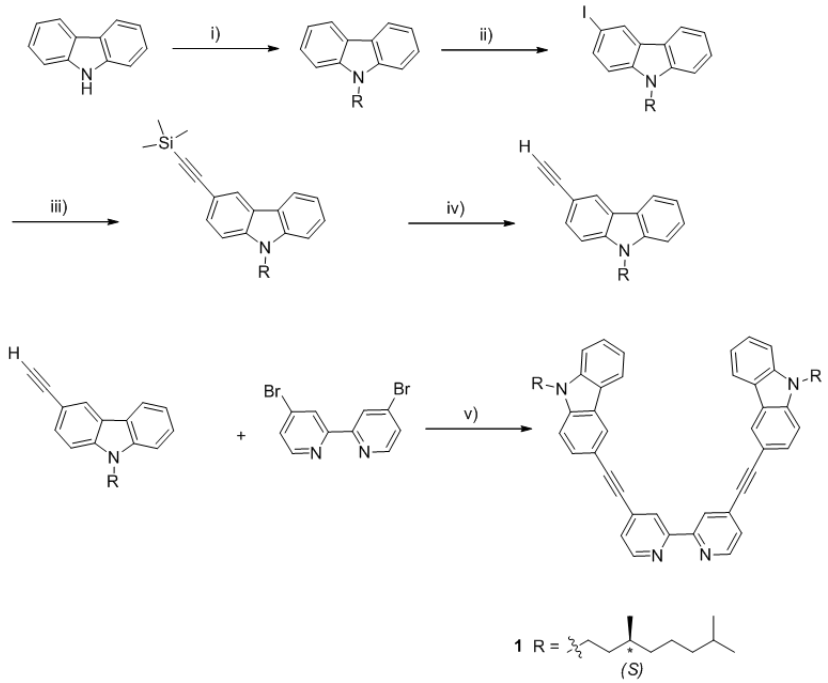
2. Yield: 62%; ^{1}H NMR ($CDCl_3$, 300 MHz):δ 8.58-8.50 (br, 18H, ArH), 8.39 (br, 18H, ArH), 7.63-7.38 (br, 42H, ArH), 4.35 (br ,

12H, NCH_2), 1.84 (br, 6H, NCH_2CH), 1.6 (br, 22H, CH_2,CH), 1.18 (br, 32H, CH_2), 0.96 (br, 18H, $CHCH_3$),0.77 (br, 36H, $CH(CH_3)_2$); MALDI-TOF: Calcd for $C_{226}H_{204}Br_2N_{20}$ (n = 6), 3359.98; found 3361.35 (2852.22 for n = 5 and 2345.98 for n = 4); GPC (Polystyrene, THF): Mn = 3105 g/mol.



MALDI-TOF mass spectrum of **2**.Isotopic distribution pattern is shown in the inset.

2b) Synthesis of model derivative



Scheme 2: Synthesis of **1**. Reagents and conditions; i) RBr, NaH, THF-DMF, rt, 1 h, ii) NIS, $CHCl_3$, AcOH, rt, 16 h , iii) TMS-acetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, iv) KF, THF-MeOH, rt, v) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, 64 °C.

Synthesis of 1

i)(*S*)-9-(3,7-dimethyloctyl)-9H-carbazole: To a stirred solution of carbazole (6 g, 36 mmol) in a mixture of THF and DMF (3:1 v/v, 40 mL) was added (*S*)-1-bromo-3,7-dimethyloctane (8 g, 36 mmol) at room temperature. NaH (60% in oil 2.16 g, 54 mmol) was gradually added to the solution and stirred for 1 h. Methanol was added to quench the remaining NaH, and the solvent was evaporated. The residue was extracted with CH_2Cl_2 and the organic layer was washed with 3N aq. HCl, H_2O, dried with Na_2SO_4. The solvent was evaporated and purified by column chromatography (hexane only) gave an oily liquid. Yield: 97%; ^{1}H NMR ($CDCl_3$, 300MHz): δ 8.09 (d, J = 6 Hz, 2H, ArH), 7.48-7.37 (m, 4H, ArH), 7.23-7.19 (m, 2H, ArH), 4.30 (m , 2H, NCH_2), 1.5 (m, 4H, NCH_2CH_2), 1.21 (m, 6H, CH_2), 1.15 (m, 3H, CH_2), 0.85 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 140.37, 125.51, 122.77, 120.28, 119.57, 118.63, 109.17, 108.60, 41.26, 39.15, 37.04, 35.49, 30.85, 27.90, 24.58, 22.63, 22.56, 19.70; FAB-MS (m/z): calcd for $C_{22}H_{29}N$, 307.23, found 307.57.

ii) (*S*)-9-(3,7-dimethyloctyl)-3-iodo-9H-carbazole: A mixture of (*S*)-9-(3,7-dimethyloctyl)-9H-carbazole(8 g, 26.05 mmol) and NIS (5.8 g, 26.05 mmol) was stirred in a mixture of $CHCl_3$ (100 mL) and acetic acid (30 mL) at rt for 16 h. $CHCl_3$ was evaporated and the solution was poured to water. The resulting precipitate was collected and dissolved in $CHCl_3$. The organic layer was washed with saturated Na_2SO_3, NaCl, dried with Na_2SO_4 White solid was obtained. Yield: 85%; ^{1}H NMR ($CDCl_3$, 300 MHz):δ 8.38 (d, J = 7.8 Hz, 1H, ArH), 8.03 (d, 1H, ArH), 7.71-7.66 (dd, 1H, ArH), 7.50-7.31 (m, 2H, ArH), 7.24-713 (m, 2H, Ar), 4.26 (t , J = 7Hz, 2H, NCH_2), 1.57 (m, 4H, NCH_2CH_2), 1.20 (m, 6H, CH_2), 1.11 (m, 3H, CH_2), 0.88 (t, 6H, CH_3); ^{13}C NMR($CDCl_3$, 75 MHz):δ 133.7, 129.1, 126.2, 121.5, 120.4, 120.3, 119.2, 110.7, 108.8, 81.0, 43.1,

31.8, 29.48, 29.45, 29.2, 28.8, 27.2, 22.6, 14.0; FAB-MS (m/z): calcd for $C_{22}H_{28}IN$,433.13, found 433.33.

iii)(*S*)-9-(3,7-dimethyloctyl)-3-((trimethylsilyl)ethynyl)-9H-carbazole: Application of Sonogashira's general procedure for alkyne coupling (*S*)-9-(3,7-dimethyloctyl)-3-iodo-9H-carbazole (2.5 g, 5.77 mmol), TMS-acetylene (0.57 g, 5.77 mmol), $Pd(PPh_3)_2Cl_2$ (0.201 g, 0.288 mmol), CuI (0.054 g, 0.288 mmol) in triethylamine (5 mL) and THF (30 mL) at room temperature gave the product as yellow oil. Yield: 99%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (s, 1H, ArH), 8.04 (d, J = 6 Hz, 1H, ArH), 7.57-7.54 (dd, 1H, ArH), 7.49-7.34 (m, 2H, ArH), 7.28-721 (m, 2H, Ar), 4.27 (t , J = 7 Hz, 2H, NCH_2), 1.51 (m, 4H, NCH_2CH_2), 1.20 (m, 6H, CH_2), 1.15 (m, 3H, CH_2), 0.85 (t, 6H, CH_3), 0.29 (s, 9H, $SiCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.59, 140.30, 129.74, 126.02, 124.55, 122.47, 120.35, 119.01, 112.99, 108.59, 106.56, 91.55, 41.23, 39.15, 37.07, 35.46, 30.84, 27.90, 24.57, 22.64, 22.56, 19.69, 0.21; FAB-MS (m/z): calcd for $C_{27}H_{37}NSi$, 403.67, found 403.55.

iv)(*S*)-9-(3,7-dimethyloctyl)-3-ethynyl-9H-carbazole: To a solution of(*S*)-9-(3,7-dimethyloctyl)-3-((trimethylsilyl)ethynyl)-9H-carbazole (1.5 g, 4.95 mmol) in THF was added a solution KF (1 g, 4.95 mmol) in methanol. After stirring at room temperature for 1 h solvent was evaporated and the residue was extracted with $CHCl_3$. The organic layer was washed with H_2O and dried (Na_2SO_4).The crude product was purified by column chromatography to give the product as yellow oil. Yield: 96%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (s, 1H, ArH), 8.05 (d, J = 6 Hz, 1H, ArH), 7.6-7.56 (dd, 1H, ArH),7.49-7.35 (m, 2H, ArH), 7.28-7.20(m, 2H, Ar), 4.27 (t, J = 7Hz, 2H, NCH_2), 3.06 (s, 1H, CH), 1.5 (m, 4H, NCH_2CH_2), 1.21 (m, 6H, CH_2), 1.15 (m, 3H, CH_2), 0.85 (t, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$):δ 140.7, 129.5, 126.1, 124.6, 120.4, 119.3, 111.8, 108.9, 108.6, 85.0, 43.1, 31.8, 29.4, 29.3, 29.2, 28.9,

27.2, 22.6,14.0; FAB-MS (m/z): calcd for $C_{24}H_{29}N$, 331.23, found 332.49.

v) 4,4'-bis((9-((S)-3,7-dimethyloctyl)-9H-carbazol-3-yl)ethynyl)-2,2'-bipyridine (1): 4,4'-Dibromo-2,2'-bipyridine(279 mg, 0.88 mmol), was coupled with (*S*)-9-(3,7-dimethyloctyl)-3-ethynyl-9H-carbazole (582 mg,1.76 mmol) in presence of $Pd(PPh_3)_2Cl_2$ (30 mg, 0.044 mmol), CuI (8 mg, 0.044 mmol) in triethylamine (5 mL) and THF (30 mL) by the application of Sonogashira's general procedure for coupling under reflux condition. The crude product obtained was purified by column chromatography in basic alumina using EtOAc/Hexane (2:8). Yield: 67%; mp. 165-166 $^{\circ}C$; FT-IR (KBr)ν_{max} 2920, 2846, 2197, 1626, 1581, 1478, 1231, 1133, 836, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.63 (d, 2H, ArH), 8.5 (s, 2H, ArH), 8.27 (s, 2H, ArH), 8.06-8.03 (d, 2H, ArH), 7.68-7.58 (dd, 2H, ArH), 7.46-7.31 (m, 8H, ArH), 7.23-7.18 (m, 2H, ArH), 4.34 (t , J = 7Hz, 4H, NCH_2), 1.86 (m, 2H, CH_2), 1.63 (m, 8H, CH_2), 1.23 (m, 2H, CH), 1.12 (m, 8H, CH_2), 1.06 (m, 6H, CH_2), 1.02-0.83 (m, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$):δ 153.0, 149.18,140.72 129.53, 126.29, 125.28, 124.68, 123.13, 120.61, 119.56,117.05, 114.47 112.04, 108.89, 104.01, 85.63, 80.02,53.05, 41.40, 39.19,37.09, 35.57, 30.92, 29.69, 27.93, 24.61 22.65,19.75; FAB-MS (m/z)$[M+H]^+$: calcd for $C_{58}H_{62}N_4$, 816.14, found 816.45.

3 Details of photophysical study

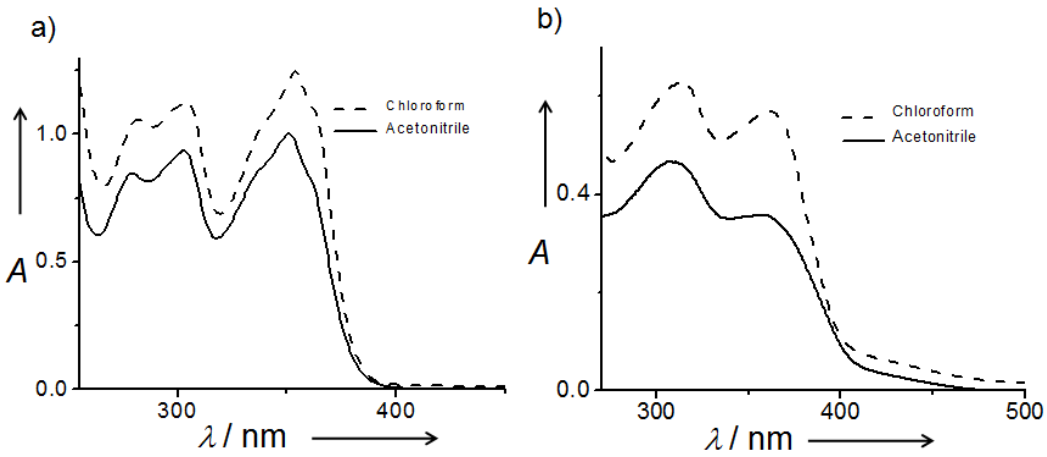


Figure S1. Absorption spectra of a) **1**(1.6 × 10^{-5} M) and b) **2** (3 × 10^{-6} M) chloroform and acetonitrile.

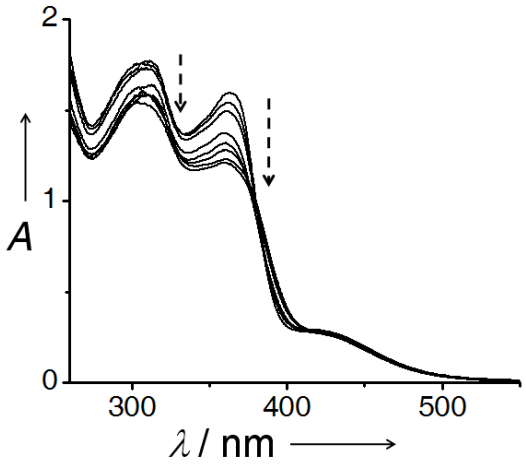


Figure S2. Absorption changes of **2** [8 × 10^{-6} M] in varying percentages of acetonitrile in chloroform (0-90%, v/v).

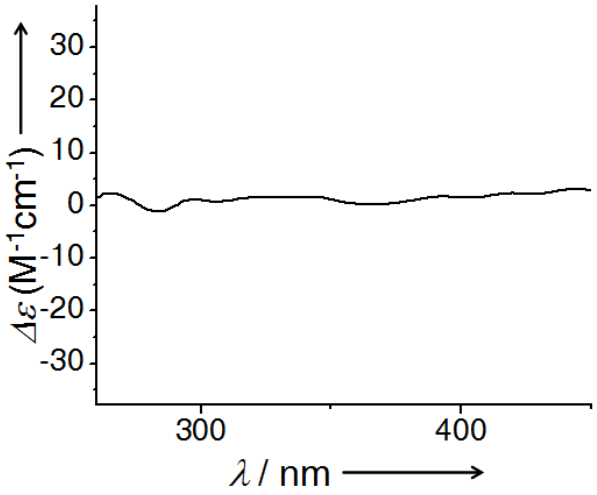


Figure S3. a) CD spectrum of **2** in chloroform (8 x 10^{-6} M)

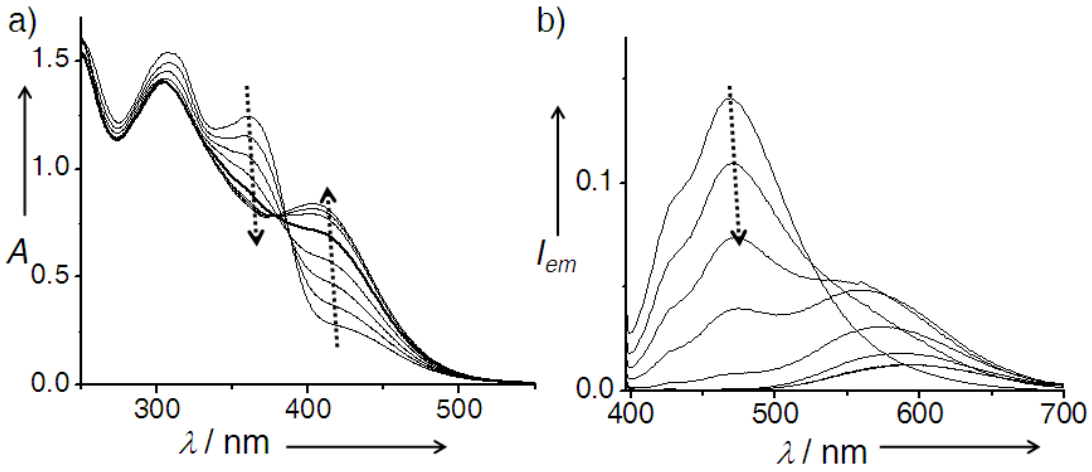


Figure S4. a) Changes in the absorption and b) emission spectra of **2** (8 × 10^{-6} M) upon addition of Zn^{2+} (0–2.6 x 10^{-5} M) in 60% acetonitrile/chloroform solution.

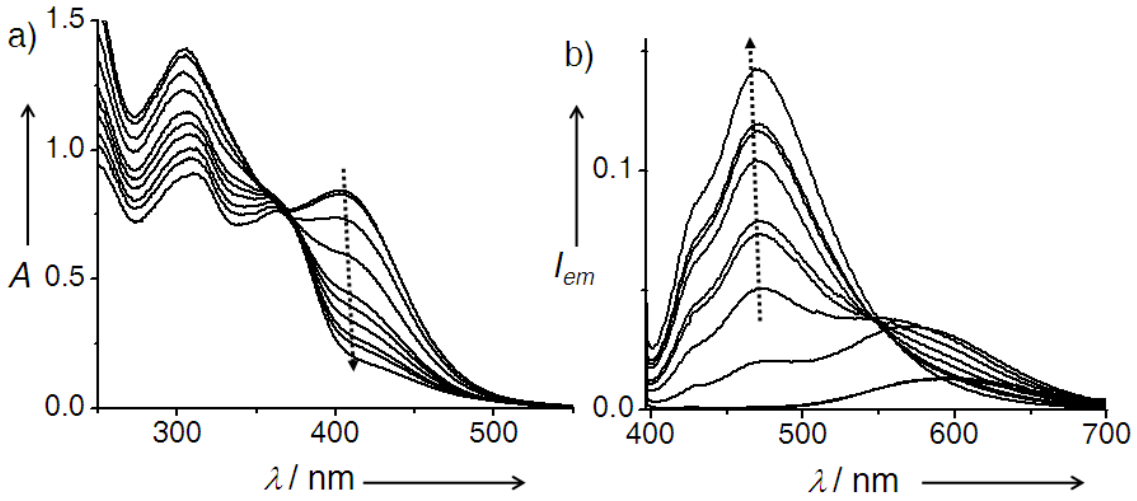


Figure S5. a) Changes in the absorption and b) emission spectra of zinc complexed **2** (8 × 10^{-6} M) upon addition of EDTA (0–3.3 x 10^{-5} M) in 60% acetonitrile/chloroform solution.

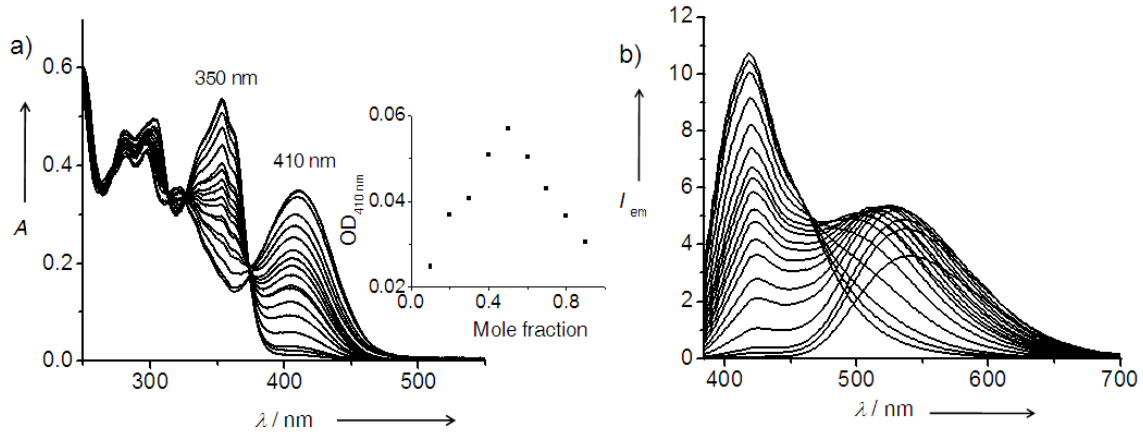


Figure S6. a) Changes in the absorption and b) emission spectra of **1** (6 × 10^{-6} M) upon addition of Zn^{2+} (0–2.6 x 10^{-5} M) in chloroform solution. (Job's plot for 1:1 binding is shown in inset)

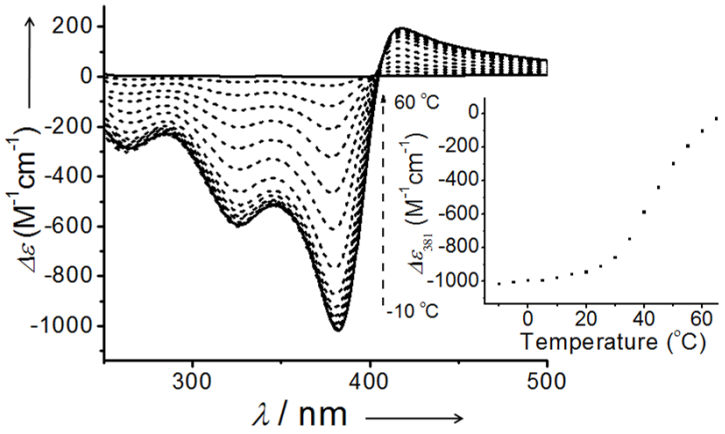


Figure S7. Changes in the CD spectrum of **2** (8 × 10^{-6} M) with temperature at 60% acetonitrile/chloroform (v/v) solution. Inset shows the changes in CD intensity at 382 nm with temperature

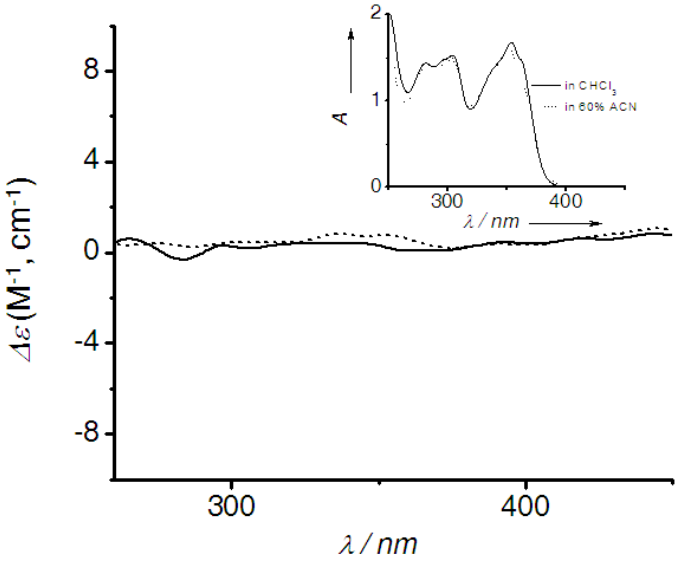


Figure S8. CD spectra of **1**(2.5 × 10^{-5} M in Chloroform (—) and 60% Acetonitrile (……).*Inset figure shows the corresponding absorption spectra.*

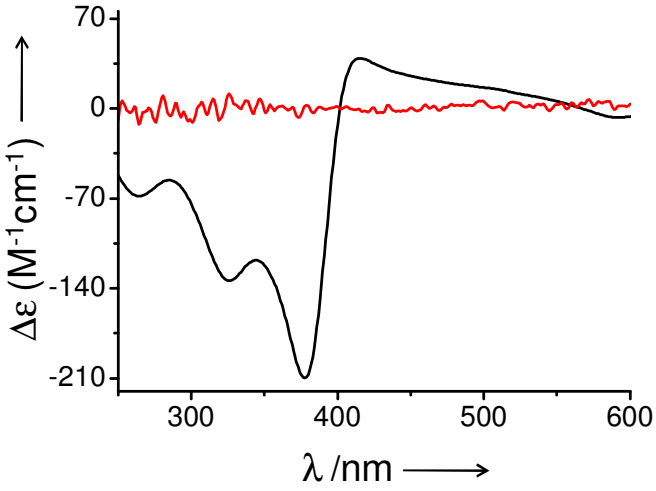


Figure S9. CD spectra of **oligomer with 4 repeat units** (—) and **oligomer with 3 repeat units** (—) in 60% Acetonitrile. Oligomer with 4 repeat units is CD active while oligomer with 3 repeat units is CD silent.

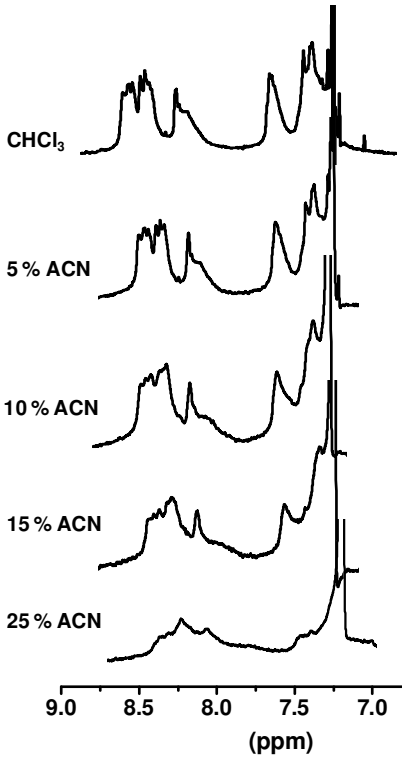


Figure S10. Partial ^{1}H NMR spectral changes (500 MHz at 25 °C) of oligomer **2** in varying percentages of acetonitrile in chloroform (0–25%, v/v)

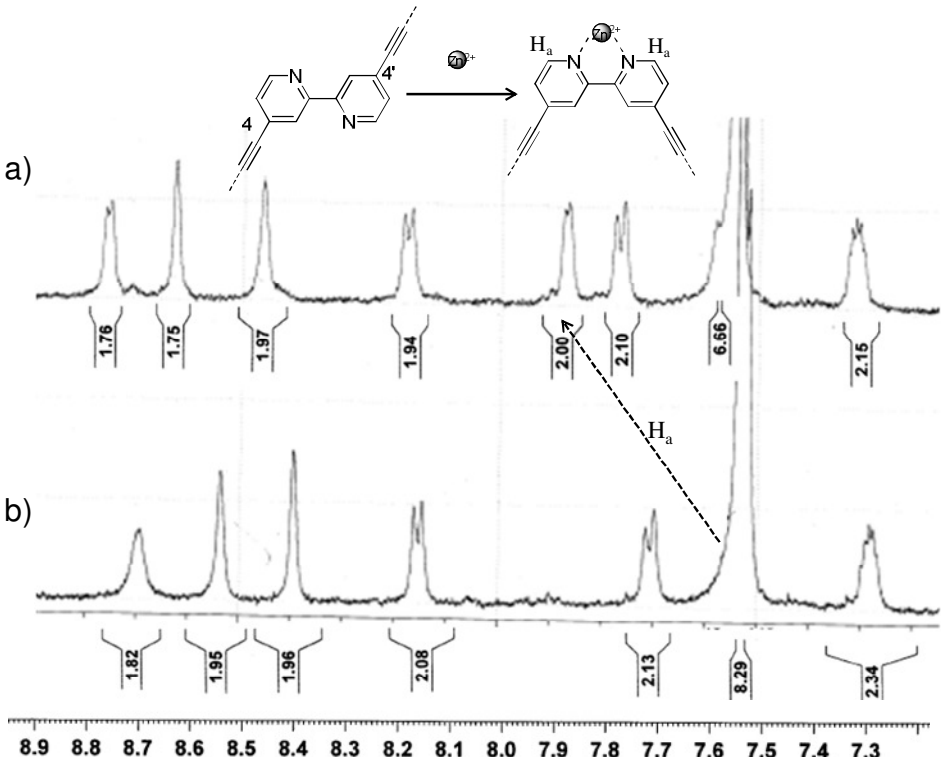


Figure S11. Partial ^{1}H NMR spectral changes (500 MHz at 25 °C) of **1** a) after and a) before complexation with $Zn(ClO_4)_2$ in $CDCl_3$.