Controlled aggregation of conjugated polymer nanoparticles via organic acid treatments

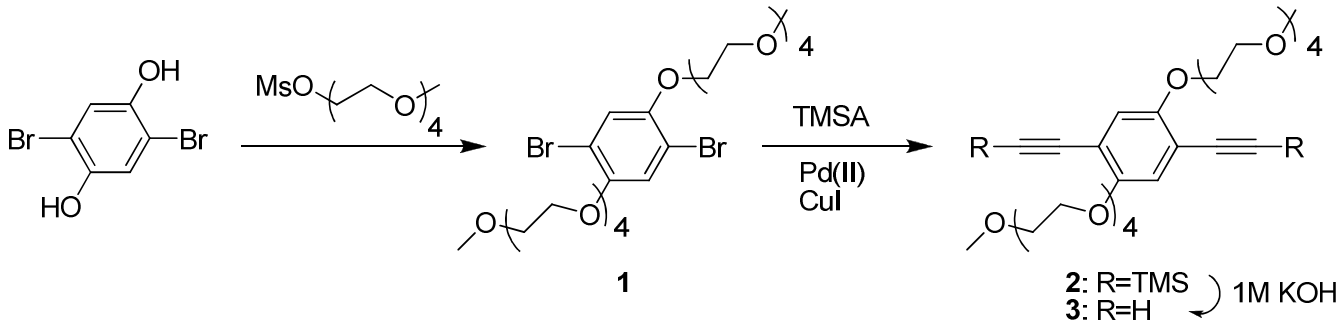
Yoon-Joo Ko, Eladio Mendez, and Joong Ho Moon*
Department of Chemistry and Biochemistry, Florida International University,
11200 SW 8th St., Miami, FL 33199
jmoon@fiu.edu

General

Chemical, including solvents, were purchased from Fisher Scientific and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Cambridge, MA). Dialysis and solvent exchange of CPNs were conducted by using an Ultrafiltration Stirred Cell (Millipore) with membrane filters (Ultracel Ultrafiltration Disc, molecular weight cut-off (MWCO): 3kDa and 10kDa). UV-vis spectra were recorded using a Varien Cary 50 Bio spectrophotometer. Fluorescence (FL) spectra were obtained using a FluoroMax-3 spectrofluometer (Jobin Yvon/Horiba). For determination of quantum yield (QY), 9,10-bis(phenylethynyl)anthracene (QY=1.0) in cyclohexane was used as a fluorescence standard. Hydrodynamic radii were determined by dynamic light scattering technique using Zetasizer nano–ZS (Zen 3600, Malvern Instruments Ltd.). NMR spectra were recorded on a 600 MHz Avance Bruker NMR spectrometer equipped with a gradient system capable of producing magnetic field pulse gradients in the z-direction of about 50 G cm^{-1}. Themical shifts are reported in parts per million (ppm) for ^{1}H NMR on δ scale based on the middle peak (δ = 4.8 ppm) of the D_2O solvent as an internal standard. All experiments were carried out using a 5 mm BBI probe and the temperature was 298K. The mixing time was 300ms at NOE measurement.

Synthesis

A) Synthesis of 13,13'-(2,5-diethynyl-1,4-phenylene)bis(oxy)bis(2,5,8,11-tetraoxatridecane) (3).



13,13'-(2,5-dibromo-1,4-phenylene)bis(oxy)bis(2,5,8,11-tetraoxatridecane) (1) : A suspension of 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethyl 4-methylbenzenesulfonate[1] (20.6 mmol; 5.9 g), 2,5-dibromohydroquinone (10.3 mmol; 2.76g) and potassuim carbonate (103 mmol; 14 g) in 30 mL of DMF

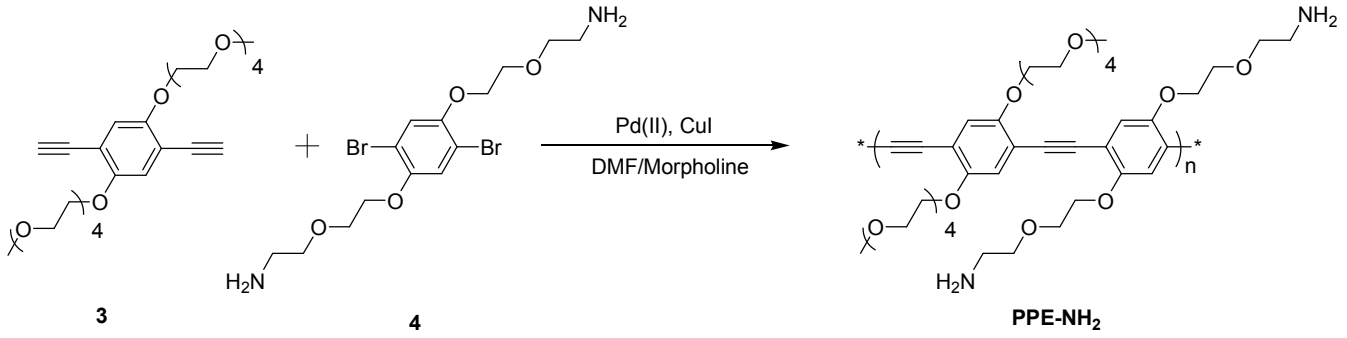
1) Gentilini, C.; Boccalon, M., Pasquato, L. Eur. J. Chem. 2008, 3308-3313.

was heated to 80°C overnight. The mixture was concentrated *in vacuo* and diluted with 50mL of dichloromethane. The solution was washed with water (20 mL × 3), dried (Na_2SO_4), and evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, ethyl acetate/ hexane (3:1, v/v)). Yield : 3.7 g (55 %). ^{1}H NMR(600MHz) : δ = 7.15 (s, 1H, Ar-H, *J* = 6), 4.12 (t, 4H, Ar-OC<u>H</u>$_2$, *J* = 6), 3.87 (t, 4H, OCH_2, *J* = 6), 3.76 (t, 4H, OCH_2, *J* = 6), 3.69-3.63 (m, 16H, OCH_2), 3.55 (t, 4H, OCH_2, *J* = 6), 3.37 (s, 6H, CH_3); 13C NMR(150MHz) : δ = 150.5, 119.4, 111.6, 72.1, 71.3, 70.9, 70.8, 70.72, 70.4, 69.8, 59.2.

(2,5-bis(2,5,8,11-tetraoxatridecan-13-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)bis(trimethylsilane) (2) : Compound **1** (5 g, 7.7 mmol) was added to a Schlenk flask fitted with a stir bar, $Pd(PPh_3)_2Cl_2$ (0.54 g, 0.77 mmol) and CuI (0.073 g, 0.39 mmol). A solution of THF (20 mL) and diisopropylamine (10 mL) was then added to the reaction mixture. Subsequently, triethylsilylacetylene (4.4 mL, 31 mmol) was added to the reaction mixture. The reaction was allowed to proceed for 12 h at 60 °C, cooled to room temperature and the solvent was evaporated. The suspension was re-dissolved with methylenechloride, washed with saturated ammonium chloride (2 ×30 mL), and then dried over magnesium sulfate. The solvent was evaporated to produce dark brown oil, which was purified by column chromatography (silica gel, ethyl acetate/ hexane (4:1, v/v)). Yield : 5 g (95 %). ^{1}H NMR(600MHz) : δ = 6.91 (s, 1H, Ar-H), 4.12 (t, 4H, Ar-OC<u>H</u>$_2$, *J* = 6), 3.87 (t, 4H, OCH_2, *J* = 6), 3.78 (t, 4H, OCH_2, *J* = 6), 3.68-3.66 (m, 12H, OCH_2), 3.64 (t, 4H, OCH_2, *J* = 6), 3.54 (t, 4H, OCH_2, *J* = 6), 3.38 (s, 6H, CH_3), 0.25 (s, 9H, $SiMe_3$); 13C NMR(150MHz) : δ = 154.0, 117.9, 114.3, 100.9, 100.4, 72.0, 71.2, 70.8, 70.7, 70.6, 69.7, 69.6, 59.0, 0.0.

13,13'-(2,5-diethynyl-1,4-phenylene)bis(oxy)bis(2,5,8,11-tetraoxatridecane) (3) : A 100 mL round-flask was charged with compound **2** (2.5 g, 3.7 mmol), 50 mL of THF and 10mL of MeOH. 1M KOH(*aq*) solution 5 mL was then added to the reaction mixture and stirred for 2h. The solvent was evaporated and the reaction mixture was purified by column chromatography (silica gel, ethyl acetate). Yield : 1.1g (90 %). ^{1}H NMR(400MHz) : δ = 7.00 (s, 1H, Ar-H), 4.15 (t, 4H, Ar-OC<u>H</u>$_2$, *J* = 6), 3.87 (t, 4H, OCH_2, *J* = 6), 3.76 (dd, 4H, OCH_2, *J* = 6), 3.73-3.63 (m, 16H, OCH_2, *J* = 6), 3.55 (dd, 4H, OCH_2, *J* = 6), 3.38 (s, 6H, CH_3, *J* = 6), 3.35 (s, 2H, CH) ; 13C NMR(150MHz) : δ = 154.1, 118.3, 113.6, 82.8, 79.6, 71.9, 71.1, 70.7, 70.6, 70.5, 69.6, 69.5, 59.0.

B) Synthesis of PPE-NH_2 and acid treatment.



A 50 mL flask under nitrogen gas was charged with the compound **3** (30 mg, 0.057 mmol), compound **4** (25 mg, 0.057 mmol), CuI (0.5 mg, 0.0028 mmol), and $Pd(PPh_3)_2Cl_2$ (3.9 mg, 0.0057 mmol). DMF (6mL)

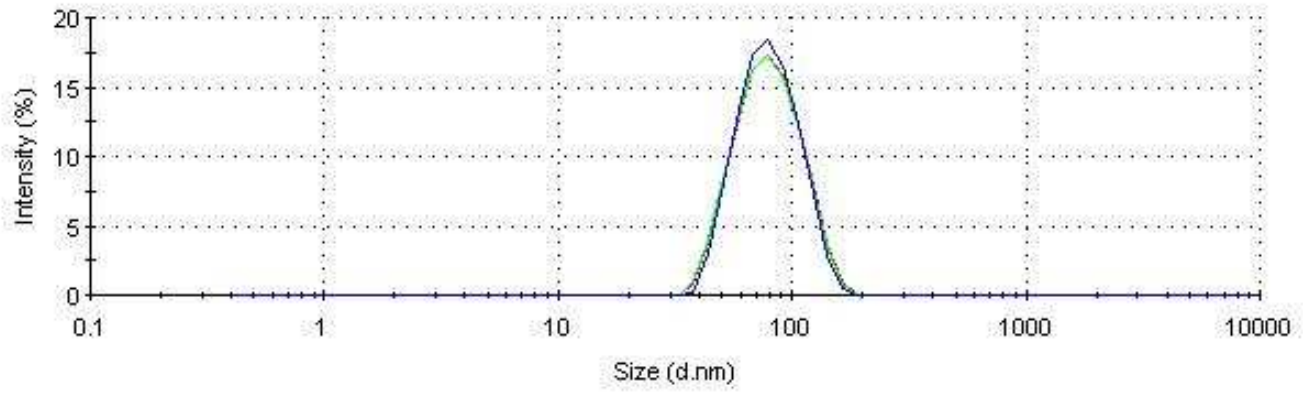
and morpholine (2 mL) were degassed and added to reaction mixture. The solution was then stirred for 16 h at 80 °C. The solution was cooled to room temperature and split into two.

3. CPN preparation and NMR sample preparation

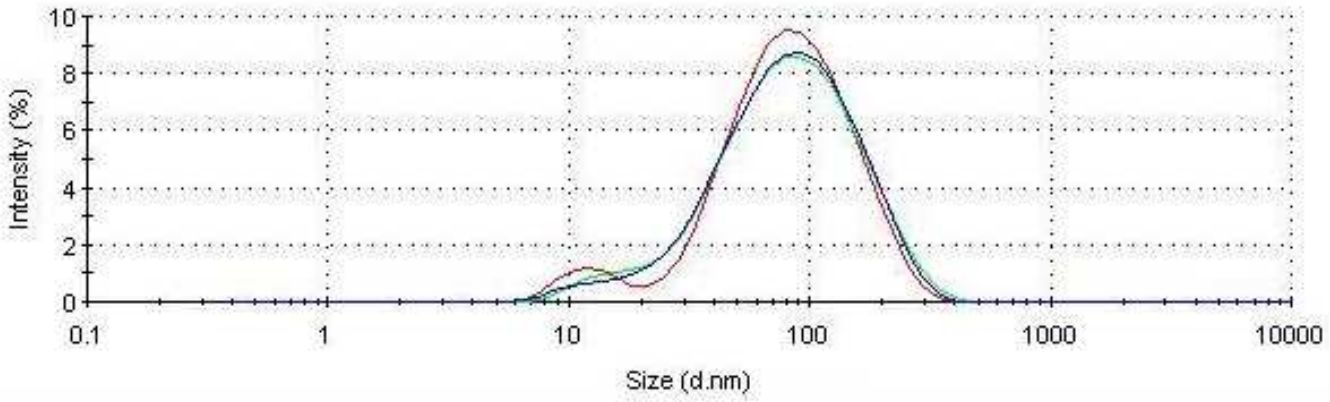
A polymer solution was divided into two solutions (~1 ml) and mixed with 10 mL of glacial acetic acid and 1M (L)-tartaric acid, respectively. Each acid solution was stirred for 10 min followed by dilution with 40mL of water, and stirred for another 10 min. Using a solvent-resistant stir cell fitted with a 10kDa-MWCO membrane, the solution was concentrated to approximately 10 mL, and dialyzed against 500 mL of water. The solution was finally concentrated to approximately 10 mL, filtered through a PTFE syringe filter (0.45 mm). The CPNs solution (10mL) was further concentrated to 1 mL, followed by addition of ~1 mL of D_2O. The CPNs solution was concentrated to 1 mL again, and additional D_2O was added. This process was repeated to 3 times.

4. Dynamic light scattering (DLS) data

A) CPN-AA

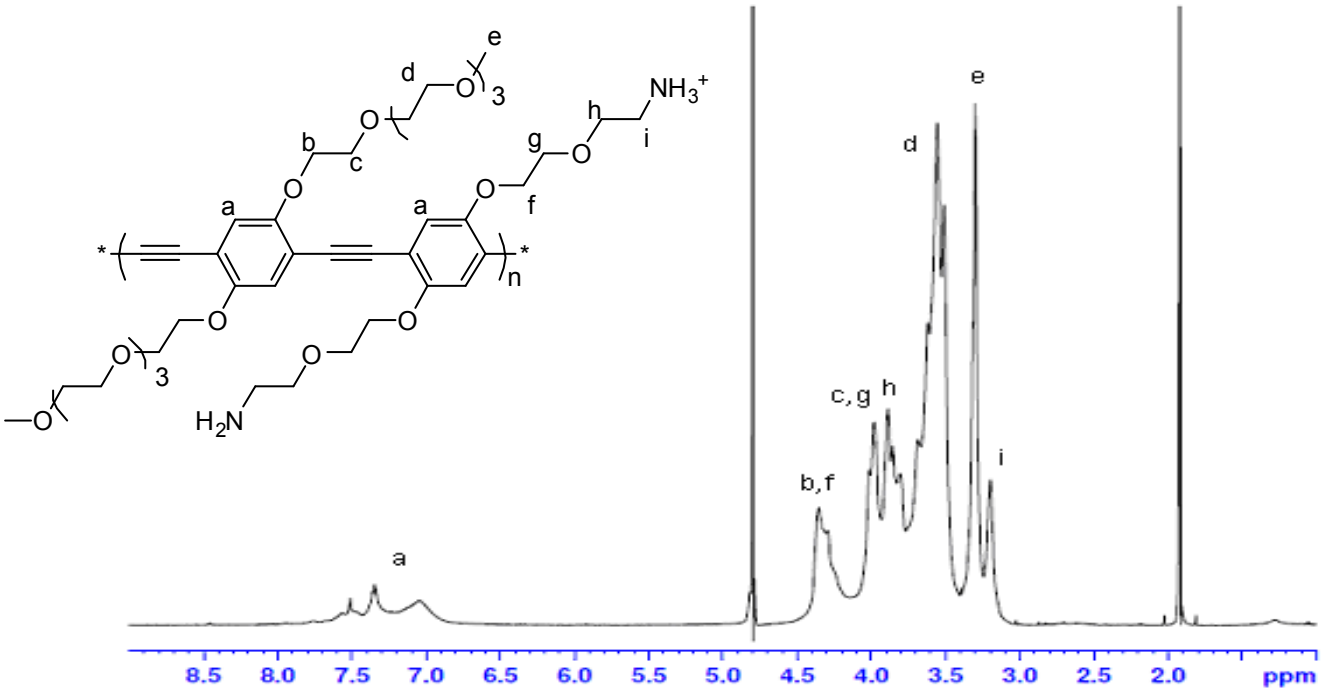


B) CPN-TA

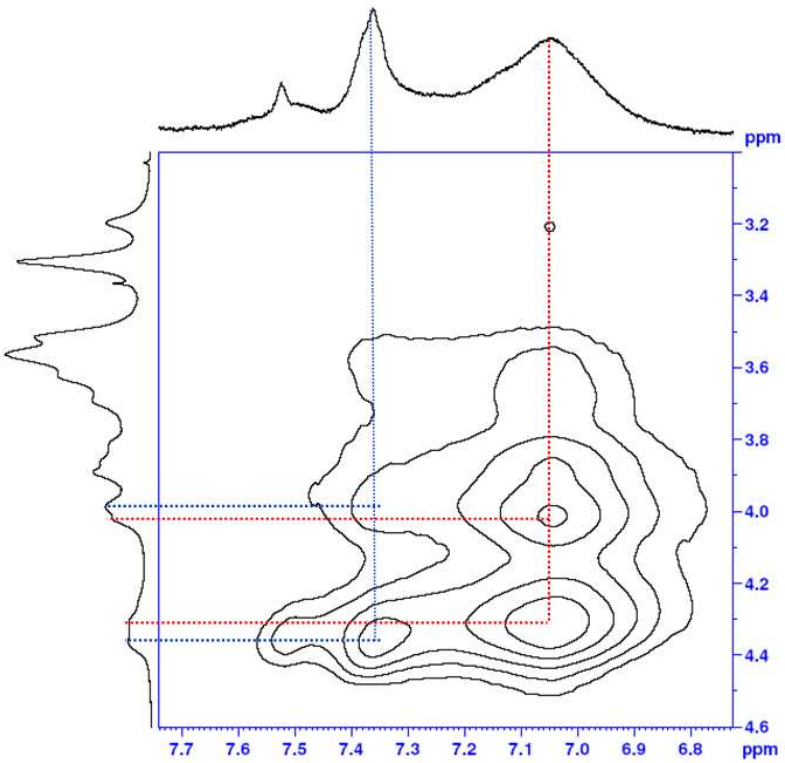


5. NMR data

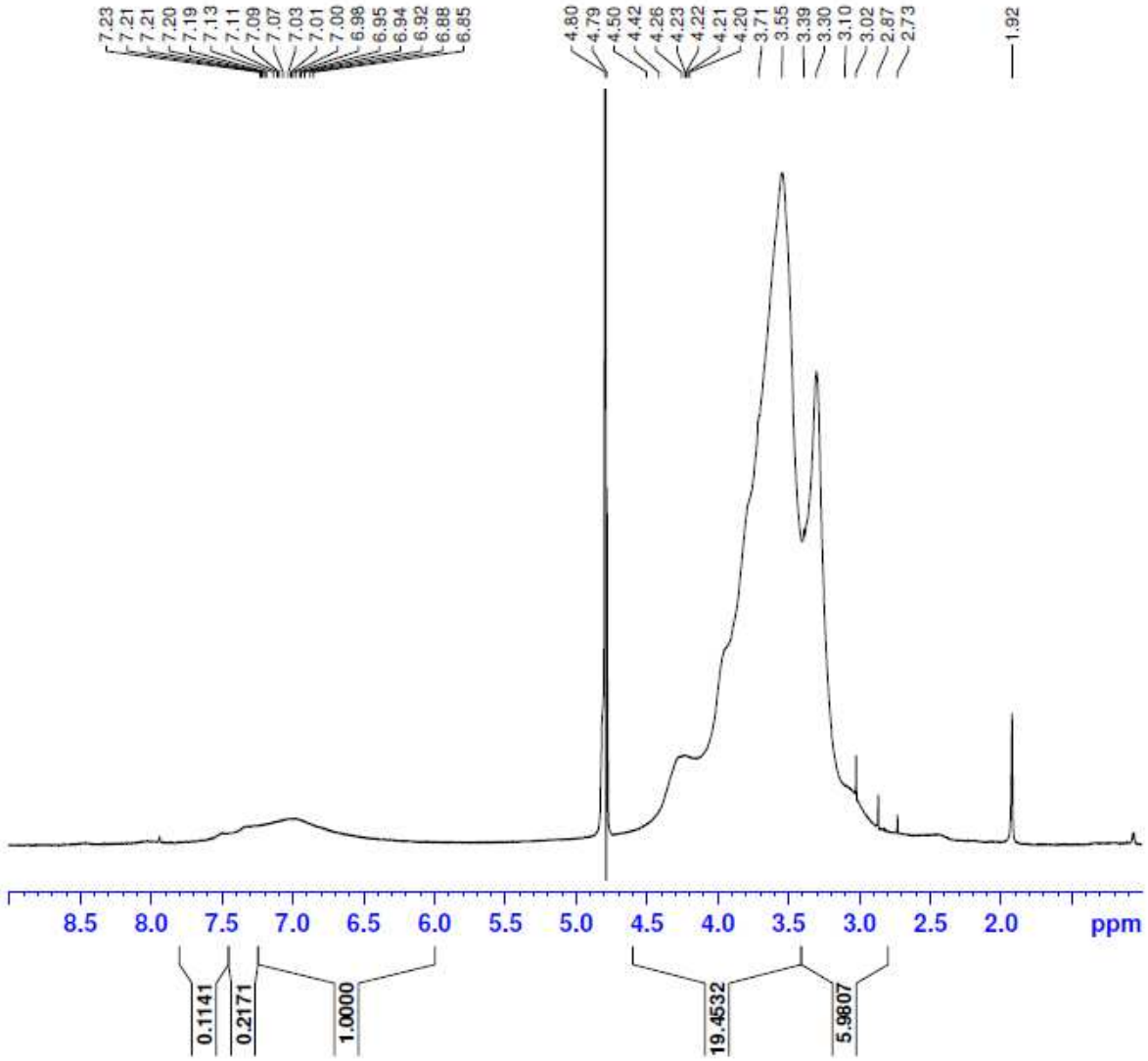
A) ^{1}H NMR spectrum of the CPN-AAs in D_2O



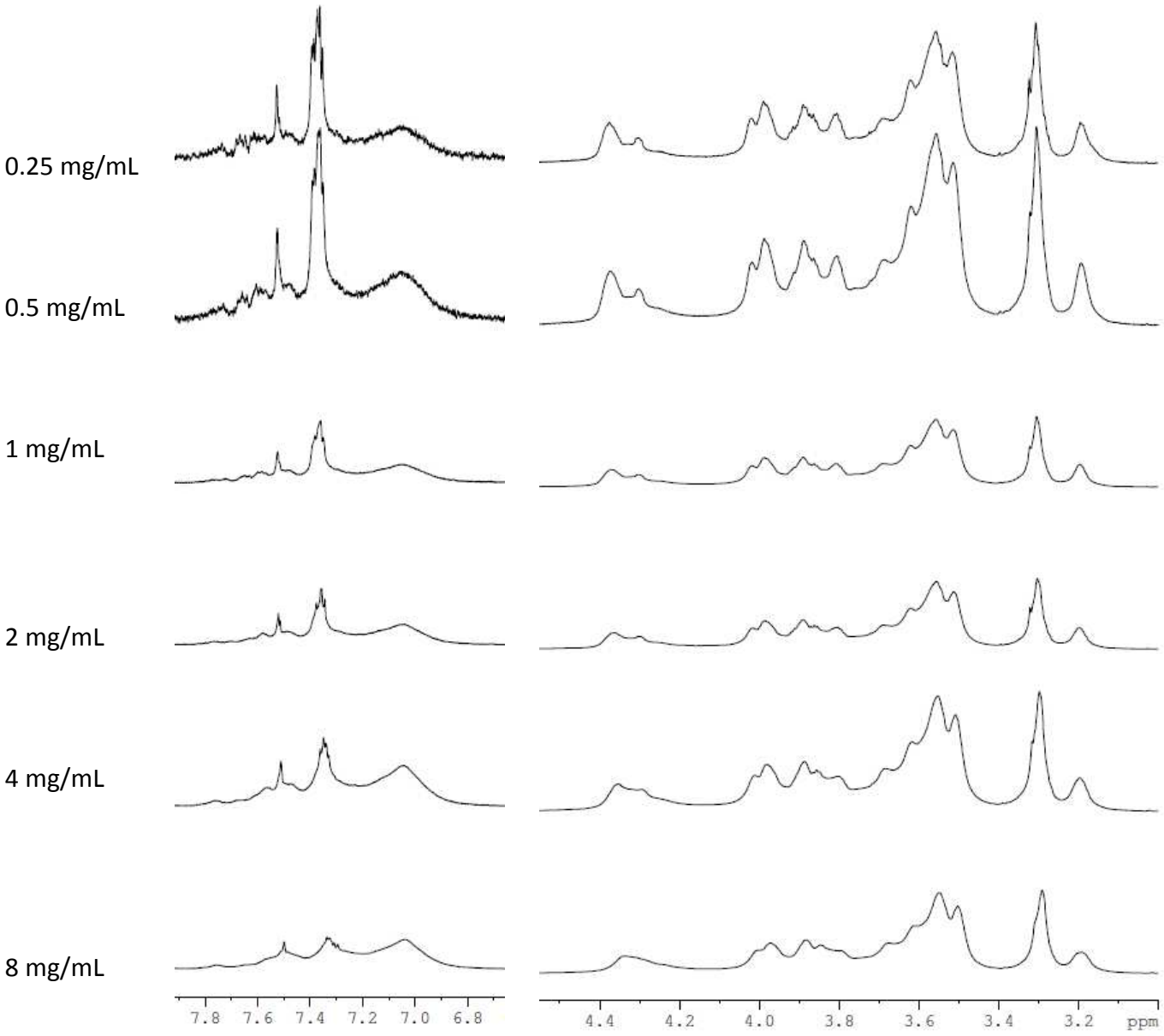
B) NOESY spectra of the CPN-AAs in D_2O



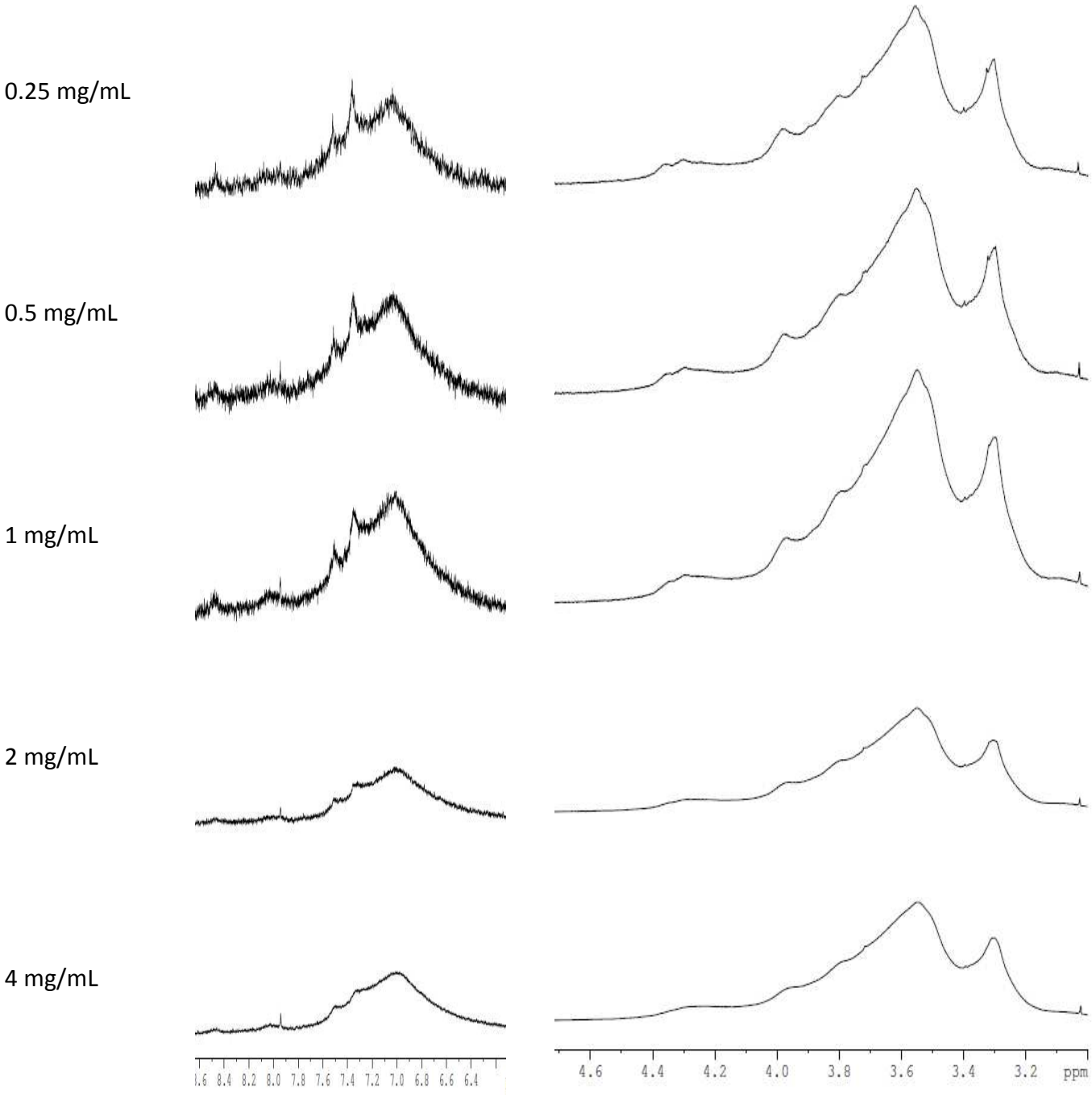
C) ^{1}H NMR spectrum of the CPN-TAs in D_2O



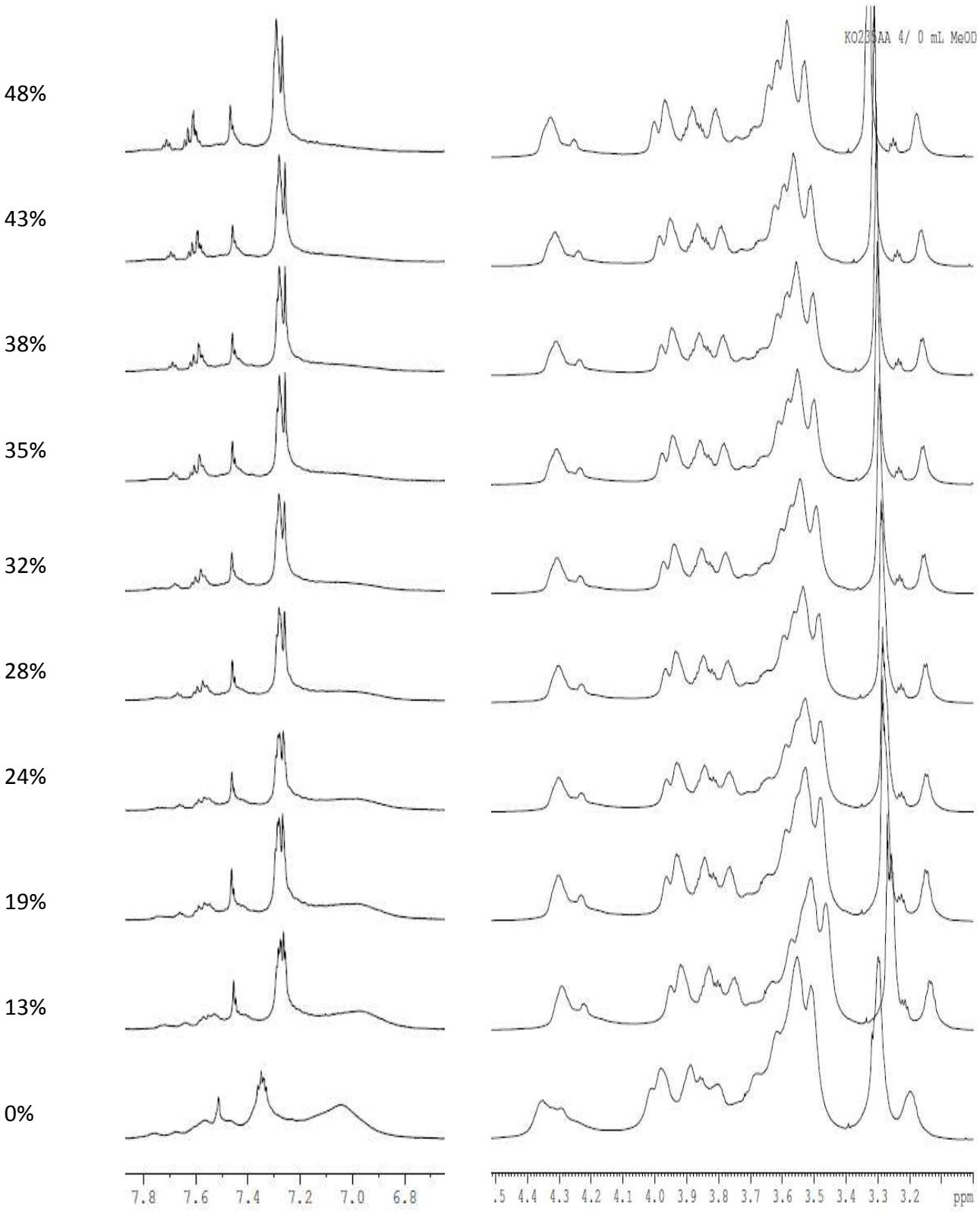
D) ^{1}H NMR spectra of CPN-AAs as a function of concentration



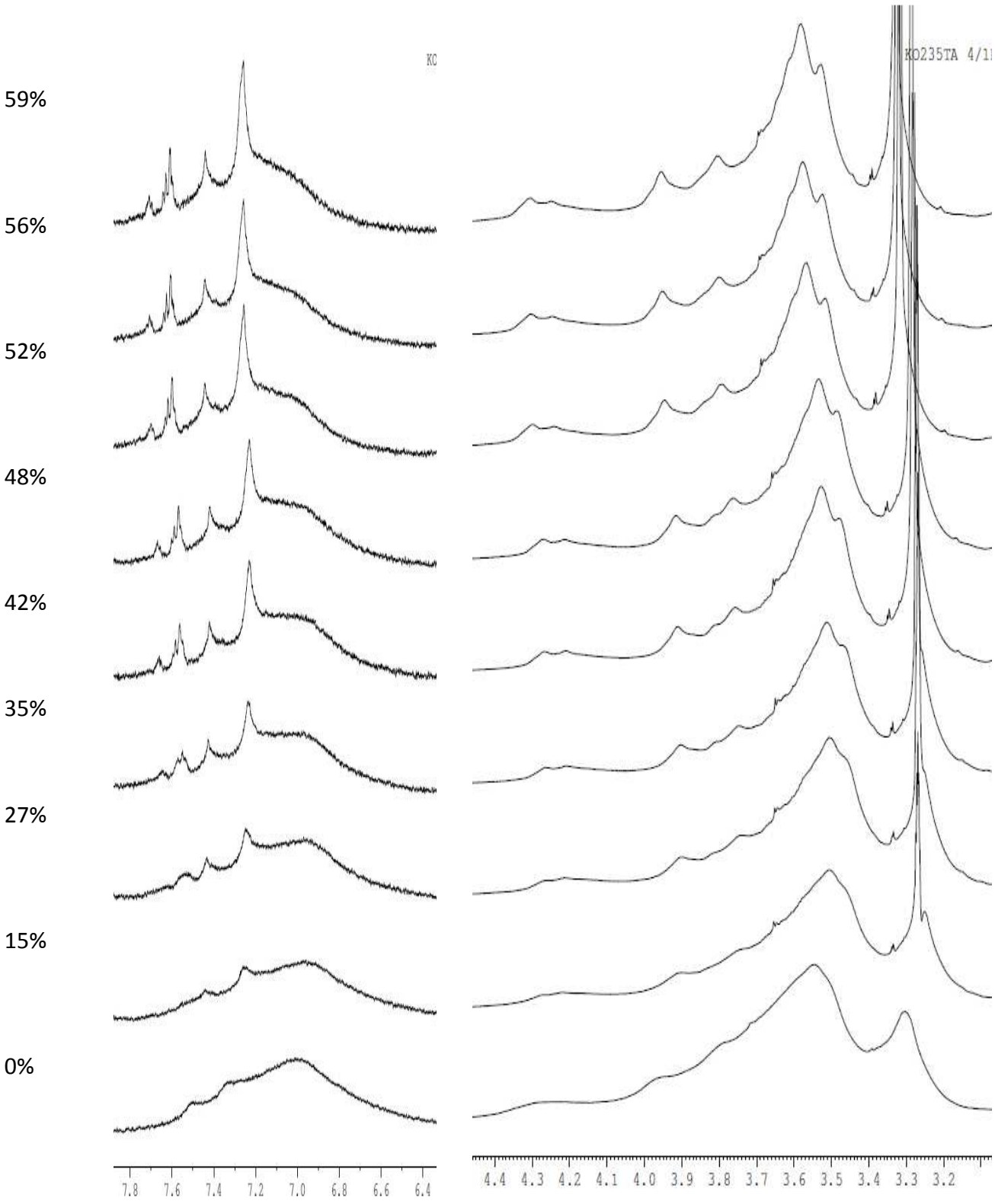
E) ^{1}H NMR spectra of CPN-TAs as a function of concentration



F) ^{1}H NMR spectra of CPN-AAs as a function of MeOD concentration



G) ^{1}H NMR spectra of CPN-TAs as a function of concentration



6. Fluorescence quenching experiment

Fluorescence intensities of the CPN solutions were measured before and after addition of mercury acetate quencher solution. Typically, 10 μL of mercury acetate solutions (2 ×10^{-4} M) in water was added to a cuvette containing 2 mL of the CPN-AA and the CPN-TAs, respectively, and fluorescence intensity at the emission maximum (485~491 nm for CPN-AAs and 491~497nm for the TA-CPNs, respectively) was recorded right after the quencher solution addition. The amount of the quencher was increased by adding additional 10 μL to the CPN solutions. The relative fluorescence intensity (Fo/F, where Fo and F are fluorescence intensities before and after addition of the quencher, respectively.) was averaged from three independent experiments and plotted as a function of the quencher concentration.