Supporting information

Halogen bond induced phosphorescence of capped γ-amino acid in solid state†

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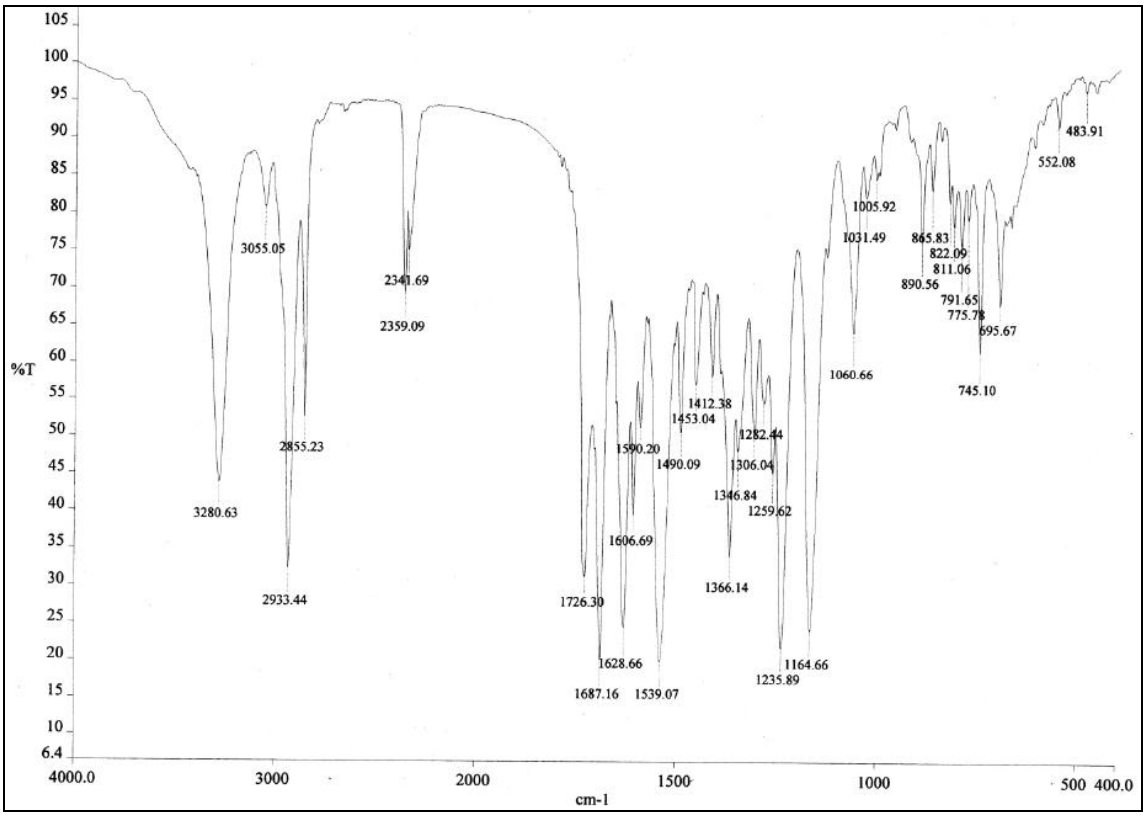
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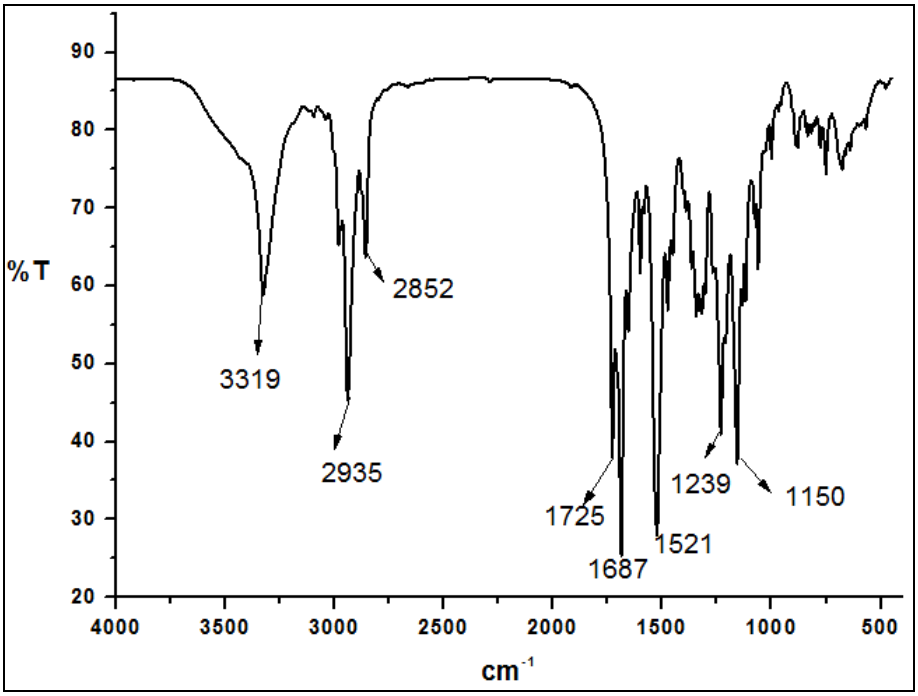
(a)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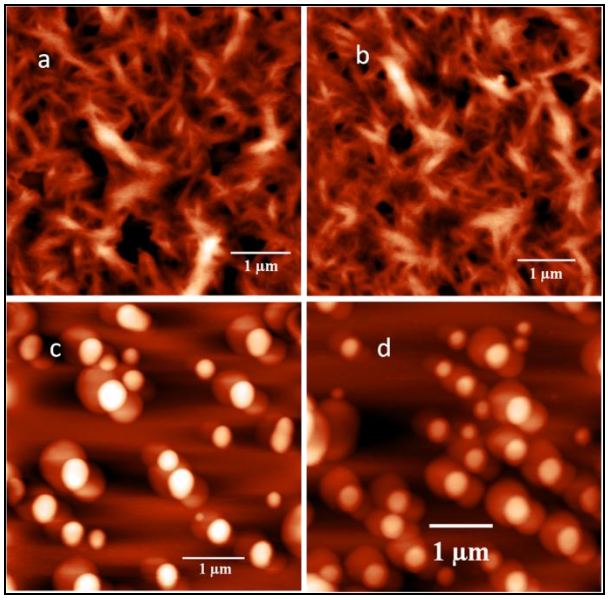
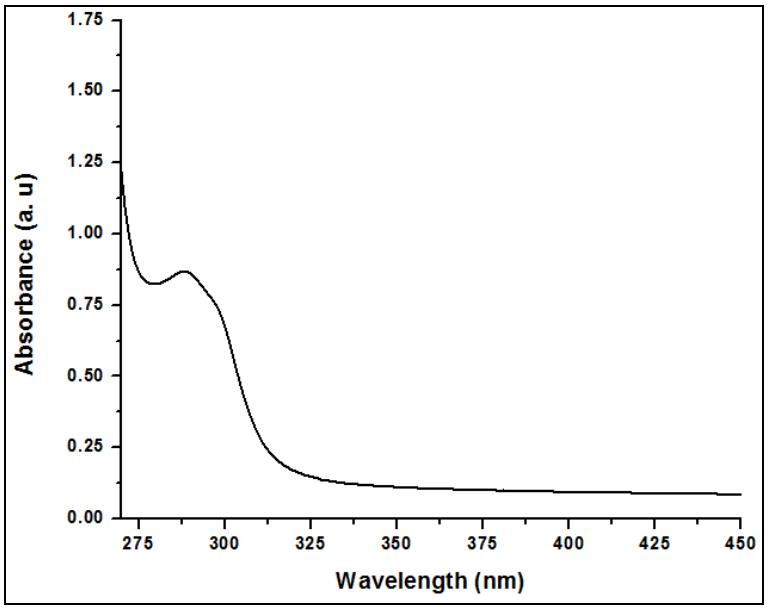
(b)

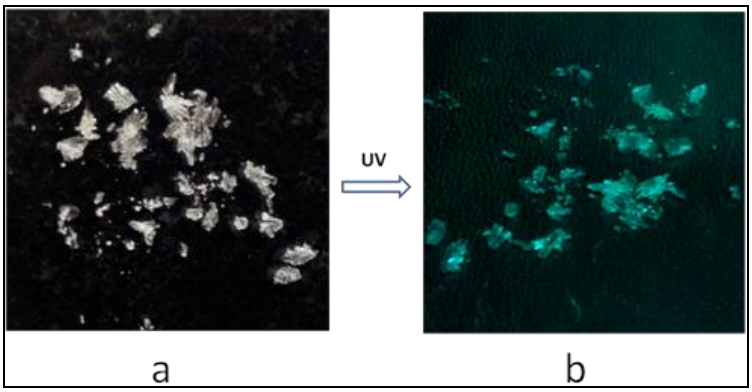
ESI Fig. 1: IR spectra of (a) foldamer **1** and (b) foldamer **2**.



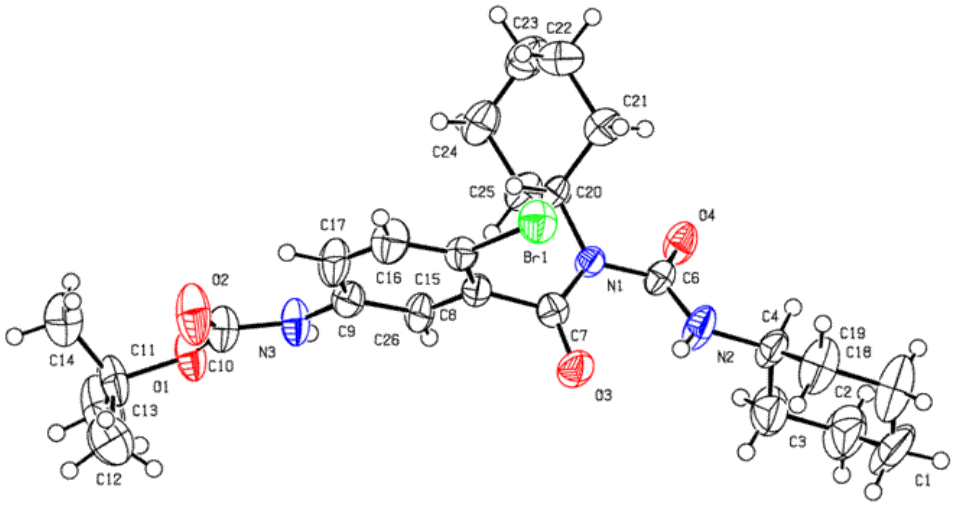
ESI Fig. 2: AFM images of foldamer **2** showing (a) and (b) the fibrillar morphology obtained from ethyl-acetate solution; (c) and (d) spherical morphology obtained from methanol solution.



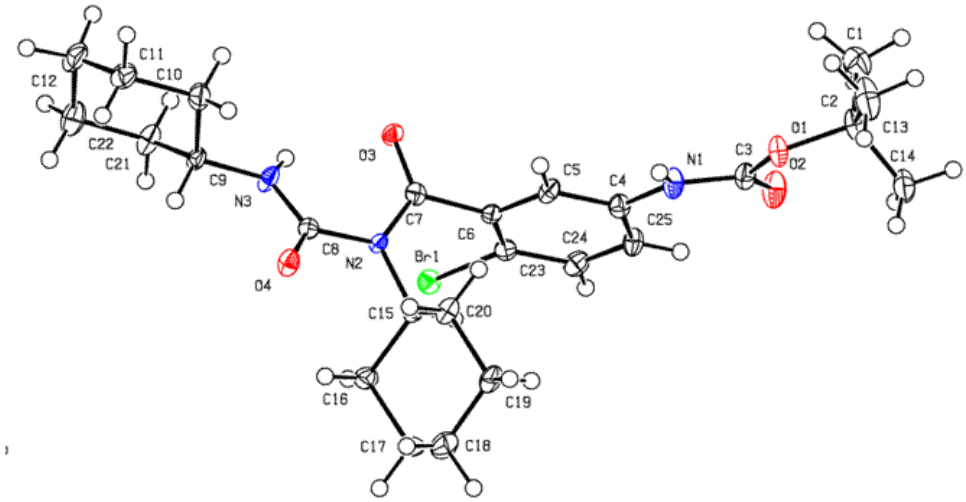
ESI Fig. 3: Absorption spectra of foldamer **2**.



ESI Fig. 4: Photographs of foldamer **1** in crystalline state (a) under laboratory light and (b) under UV light irradiation.

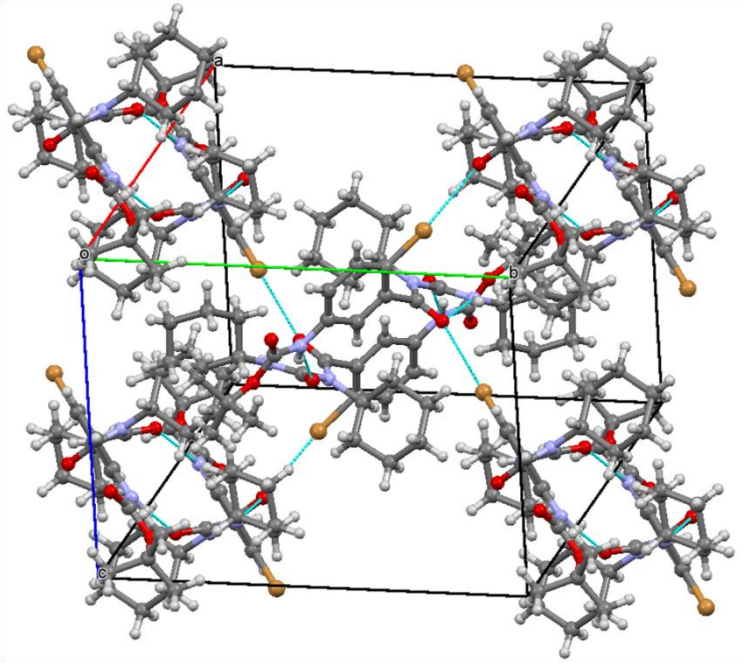


(a)

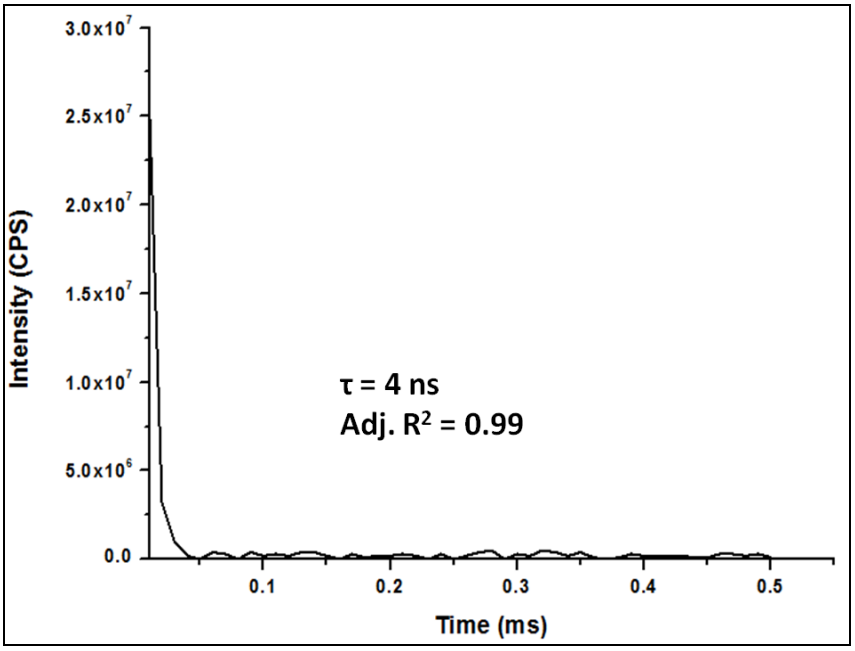


(b)

ESI Fig. 5: ORTEP diagrams of foldamer **2** with atomic numbering scheme (a) crystal obtained from ethylacetate (b) crystal obtained from methanol. 50% probability level.



ESI Fig. 6: Higher order packing of foldamer **2** via halogen bonding to form a 2D layer like structure along the crystallographic *b* direction.



ESI Fig. 7: The time resolved decay curve of the reported compound in chloroform solution.

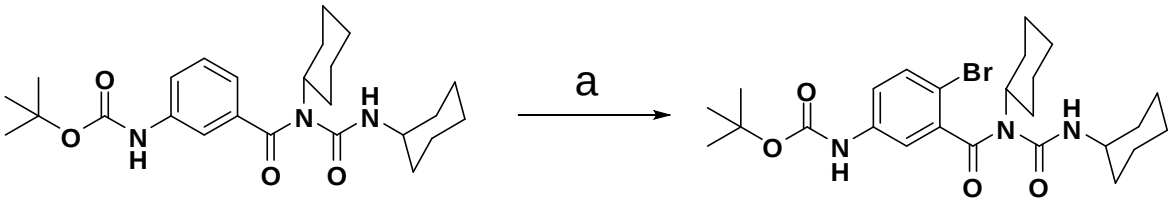


Fig. S1: Scheme 1: Reactions and conditions: (a) NBS, reflux 48 hours, chloroform.

Experimental

General methods and materials

Meta-aminobenzoic acid, *N*,*N'*-dicyclohexylurea and N-bromosuccinimide were purchased from Sigma chemicals. HOBt (1-hydroxybenzotriazole) and DCC (dicyclohexylcarbodiimide) were purchased from SRL.

Foldamer synthesis

The foldamer was synthesized by a conventional solution-phase methodology using a racemisation free fragment condensation strategy. The Boc group was used for N-terminal protection. Coupling was mediated by dicyclohexylcarbodiimide/1-hydroxybenzotriazole (DCC/HOBt). Bromination was done by refluxing the peptide in DCM with NBS. The final compound was fully characterized by 500 MHz ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and IR spectroscopy. The compound was also characterized by X-ray crystallography.

(a) Boc-Maba(Br)-DCU: 2.2 gm (5 mmol) of Boc-Maba-DCU was refluxed with 0.9 gm (5 mmol) NBS in DCM solution for 48 hours. The resulting solution was cooled and subjected to column chromatography for purification using silica gel (mesh size 100-200) and ethyl acetate: hexane (1:3) as the eluent.

Yield: 2 gm (76%)

^{1}H NMR (500 MHz, $CDCl_3$, δppm): 7.44 [2H, s, aromatic protons], 7.19 [1H, s, aromatic proton], 6.67 [1H, s, Maba NH], 3.84 [1H, s, DCU NH], 3.50 [1H, s, cyh CαH], 2.00 [1H, s, cyh CαH], 1.53-1.87 [12H, m, cyh], 1.50 [9H, s, Boc CH_3], 1.14-1.26 [8H, m, cyh]. ^{13}C NMR (125 MHz, $CDCl_3$, δppm): 152.93, 152.16, 139.03, 138.23, 133.17, 120.12, 81.23, 49.58, 28.23, 26.19, 25.36, 25.15, 24.56.

Anal. Calcd for $C_{25}H_{36}BrN_3O_4$ (521.19): C, 57.47; H, 6.94; N, 8.04.

Found: C, 57.48; H, 6.93; N, 8.05.

TOF MS *m/z*: 544.07 $[M + Na]^+$; *M*calcd: 521.19.

NMR experiments

All NMR studies were carried out Brüker AVANCE 500 MHz spectrometer at 298 K. Compound concentrations were in the range 1–10 mmol in CDCl3.

FTIR spectroscopy

All reported solid-state FTIR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique.

Atomic Force Microscopy

The morphology of the compound was investigated by atomic force microscopy (AFM). The solutions of the reported compound in ethyl-acetate and methanol (0.5 mg mL^{-1}) were drop-casted on a microscopic glass cover slip, dried under vacuum at 30°C for two days. Images were taken with an NTMDT instrument, model no. AP-0100 in semicontact-mode.

Field emission scanning electron microscopy

The morphology of the compound was investigated using field emission scanning electron microscopy (FE-SEM). The images were taken in an FE-SEM apparatus (ZEISS).

UV/Vis spectroscopy

UV/Vis absorption spectra were recorded on a Perkin Elmer UV/Vis spectrophotometer.

Photoluminescence study

Photoluminescence spectra were recorded on a FluoroMax-4 spectrophotometer (Horiba Jobin Yvon) in chloroform solution and in crystalline state obtained from ethyl-acetate and methanol.

Lifetime measurement

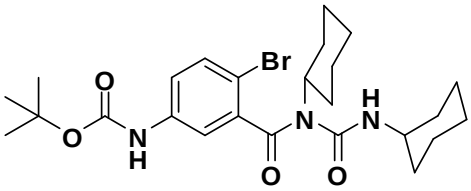
Life time of foldamer **2** in chloroform solution and in crystalline states was measured on a FluoroMax-4 spectrophotometer (Horiba Jobin Yvon). Crystals were crushed in a mortar pestle and put into the groove of the solid sample probe for lifetime measurements.

X-ray crystallography

Single crystal X-ray data were recorded on Bruker high resolution X-ray diffractometer instruments.

Mass spectrometry

Mass spectrum was recorded on a Q-Tof Micro YA263 high-resolution (Waters Corporation) mass spectrometer by positive-mode electro-spray ionization.



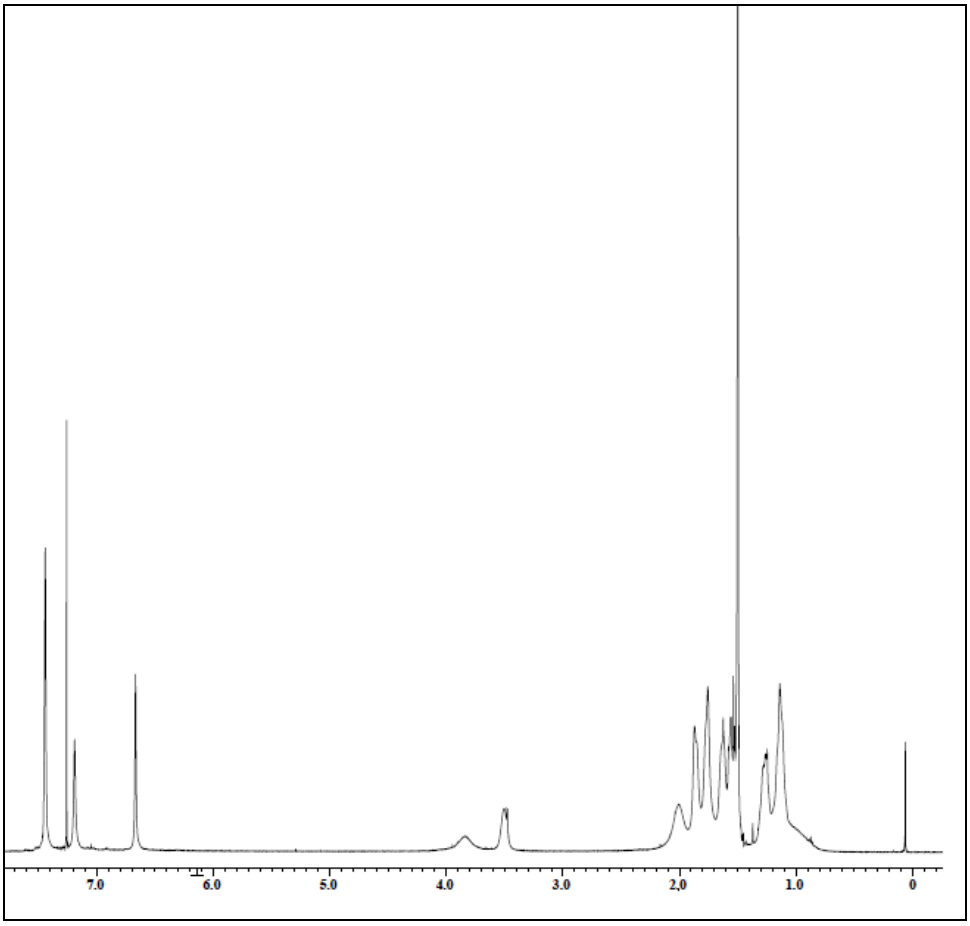
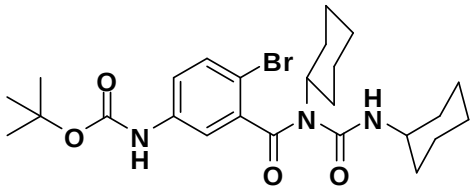


Fig. S2: ^{1}H NMR (500 MHz, $CDCl_3$, δppm) spectrum of foldamer **2.**



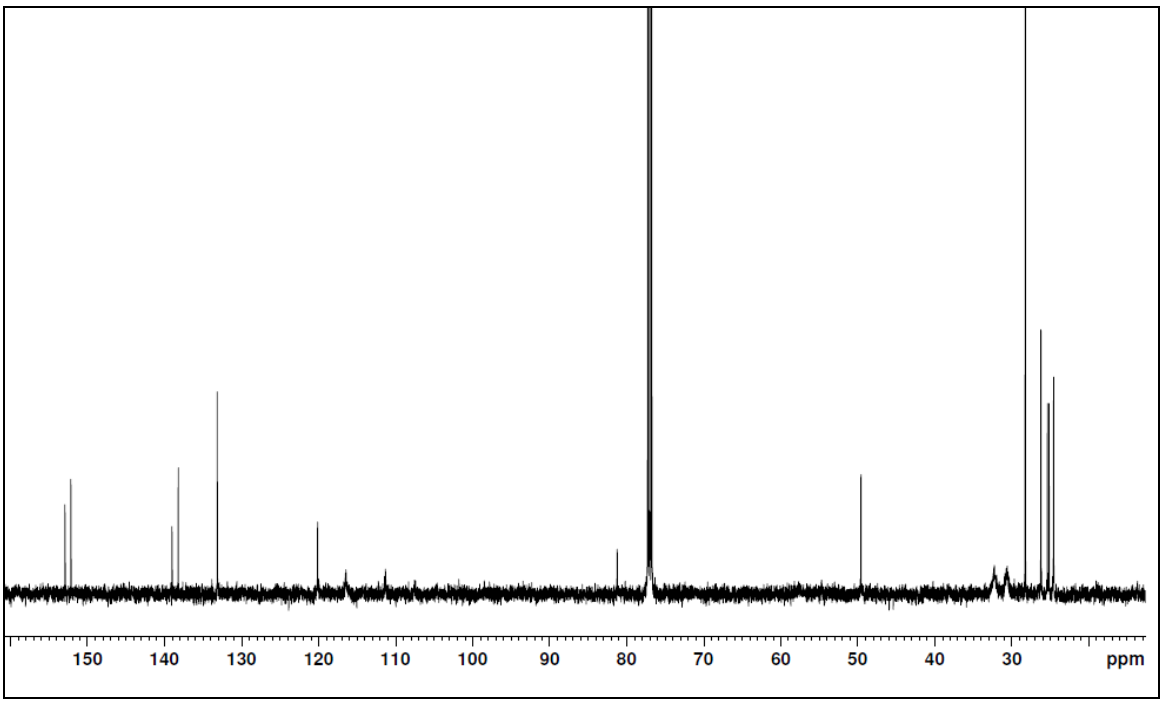
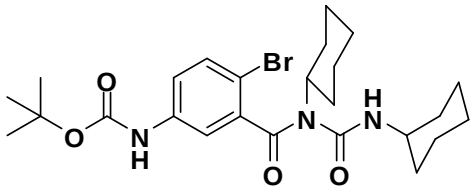


Fig. S3: ^{13}C NMR (125 MHz, $CDCl_3$, δppm) spectrum of foldamer **2.**



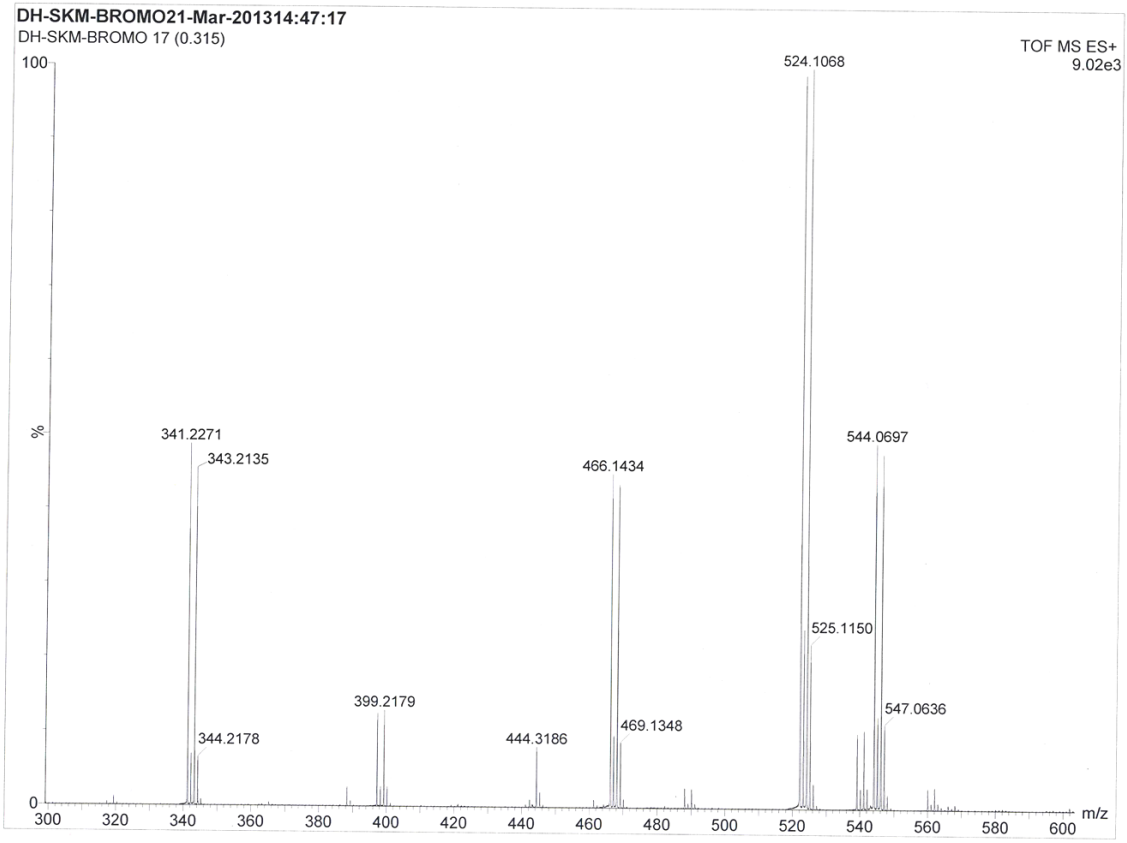


Fig. S4: Mass spectrum of foldamer **2**.

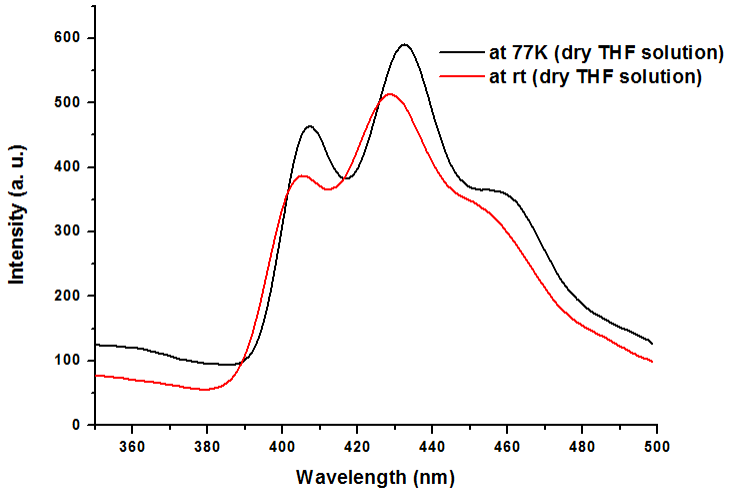


Fig. S5: Emission spectra of foldamer **2** in dry THF solution at room temperature (red) and at 77K (black).

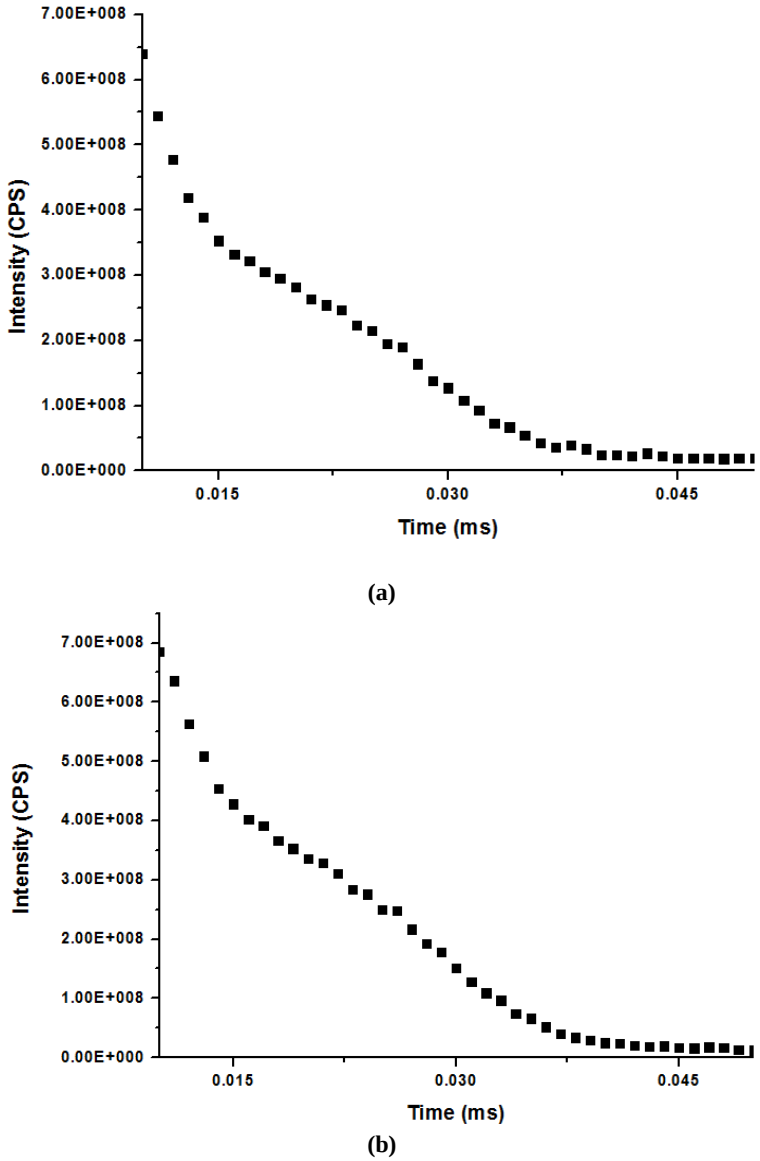


Fig. S6: The amplified decay curves of the crushed crystals obtained from (a) ethyl acetate and (b) methanol.