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ARTICLE TYPE

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

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The Boc and *N*,*N'*-dicyclohexylurea capped *p*-amino acid on monobromination showed phosphorescence in solid state. The compound exhibited different photoluminescence intensity and lifetime in crystals obtained from ethyl acetate and ¹⁰ methanol. The X-ray crystallography revealed that the intermolecular C=O....Br halogen bond direct the heavy atom effect to produce the phosphoresence.

Organic compounds are rarely phosphorescent¹ in nature because the emission from the long-lived triplet excited state ¹⁵ is non-radiative due to some inhibitory processes such as thermal perturbations, intramolecular motions, solute-solute and solute-solvent collisions, and intermolecular interactions with oxygen and humidity. Moreover, the electrons in the organic compounds are tightly bonded than that of the metal ²⁰ containing organic materials, which makes them less efficient to emit from triplet excited state.² Hence, phosphorescence is regarded mainly as a property of inorganic and organometallic compounds.³ Phosphorescent materials are commonly used in organic electronics,⁴ as well as chemical⁵ and biological

²⁵ sensing.⁶ Purely organic compounds exhibit phosphorescence under impractical conditions such as in low temperature (77 K), in rigid "glasses" of frozen solvents or inert atmospheres.⁷ Tang and co-workers have reported the crystallization induced phosphorescence of benzophenone with heavy halogen ³⁰ atoms.⁸ Kim *et. al.* have designed crystal from organic compounds with efficient phosphorescence.⁹ Kabe *et. al.* have enhanced the phosphorescence in dibenzophosphole chalcogenide mixed crystal.¹⁰ Lee and co-workers have reported the room temperature phosphorescence of metal-free ³⁵ organic materials in amorphous polymer matrices.¹¹

Previously, we have reported that the foldamer 1 containing *m*-amino benzoic acid and capped with Boc and *N*,*N*-dicyclohexylurea formed an antiparallel hydrogen bonded dimer in the solid state.¹² In this work, we present the bromo ⁴⁰ substituted capped γ -amino acid foldamer 2 that promotes the

halogen bond induced self-assembly and efficient

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, West Bengal 741252, India, Fax: 45 +913325873020; Tel: +913325873119; E-mail: <u>deba_h76@yahoo.com</u>; <u>deba_h76@iiserkol.ac.in</u> phosphorescence. In chloroform, the foldamer **2** shows very weak fluorescence. But the compound exhibits stronger photoluminescence intensity and longer lifetime in crystals obtained from methanol than ethyl acetate solution.

The foldamer **1** containing *m*-amino benzoic acid and capped with Boc and N,N'-dicyclohexylurea has been synthesized by conventional solution-phase methodology. The foldamer **2** obtained by bromination of foldamer **1** with one equivalent N-bromosuccinimide in DCM for 48 hours. The compounds were purified, characterized, and studied. The assumption was that the incorporation of heavy halogen atom, bromine would provide the halogen bonding¹⁰ which brings aromatic carbonyl and halogen atom in close proximity in crystal state. This halogen bonding joins the bromine to the cs carbonyl oxygen of neighbouring molecules in a non-covalent interaction that delocalizes the oxygen electrons partially onto the bromine, thereby amplifies triplet generation and activating triplet emission, phosphorescence.

To study the effect of bromination on self-assembly ⁷⁰ behaviour, the solid state FTIR experiments of foldamers **1** and **2** have been performed (ESI Fig. 1). Though the position and intensity of most of the peaks corresponding to NH and C=O stretching frequencies remain same for both foldamers, one of the two NHs is non hydrogen bonded in the bromo ⁷⁵ substituted foldamer **2** as the stretching frequency has shifted to higher frequency at 3319 cm⁻¹. Moreover one peak corresponding to C=O stretching frequency at 1628 cm⁻¹ has disappeared in the bromo substituted foldamer **2**.

The self-assembly and morphology of the foldamer 2 was 80 further studied by atomic force microscopy (AFM) and fieldemission scanning electron microscopy (FESEM). A solution of the corresponding compound in ethyl acetate or methanol was drop casted on clean microscopic cover slips and allowed to dry under vacuum at 30 °C for 2 days. The AFM study 85 reveals that the compound formed nanofibrillar morphology (diameter 100-150 nm) from ethyl acetate solution and spheres (diameter 300-350 nm) from methanol solution (ESI Fig. 2). FESEM images of the foldamer 2 from ethyl acetate (Fig. 1a) shows the fibrillar morphology. From methanol 90 solution the foldamer 2 exhibits spherical morphology with diameter ranging from 300-350 nm (Fig. 1b). These results demonstrate the unique property of the reported compoud to self-assemble in completely different pattern from polar aprotic (ethyl acetate) and polar protic (methanol) solvents.

[†] Electronic Supplementary Information (ESI) available: Synthesis and characterization of foldamers, ¹H NMR, ¹³C NMR, solid state FTIR spectra, Fugures ESI S1-7, Figure S1-S6. other electronic format see 50 DOI: 10.1039/b000000x/

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Fig. 1 The FESEM images of foldamer 2 from (a) ethyl acetate and (b) methanol solution showing fibrillar and spherical morphology respectively. (c) The photoluminescence spectra of the foldamer 2 in 25 chloroform solution (blue), crystals from ethyl acetate (black) and crystals from methanol (red).(d) Photographs of chloroform solution of foldamer 2 under laboratory light and under UV light. (e) and (f) showing the origin of fluorescence and phosphorescence for the compound.

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- Moreover, the bromine containing foldamer 2 exibits 30 diverse photophysical properties in solution state and in solid state. The compound has absorbance maxima at 288 nm (ESI Fig. 3). In chloroform solution the compound shows weak fluorescence having maxima at 380 nm when excited at 288 nm. But, the crystals obtained from ethyl acetate solution 35 exibit photoluminescence comprising with fluorescence similar to the solution state, as well as vibronically structured phosphorescence bands at 467, 482 and 492 nm (Fig. 1c). However, the crystals obtained from methanol solution show fluorescence with decreased intensity the and 40 phosphorescence with increased intensity (Fig. 1c). These observations can be encountered by examining the distance between the aromatic carbonyl and the bromine atom in three different cases, stated above. In solution state there is large separation between the triplet state producing aromatic
- ⁴⁵ carbonyl and the heavy atom bromine. Heavy atoms like bromine facilitates the intersystem crossing by spin-orbit coupling, thereby enhances the triplet state population and emission, the phosphorescence. Thus in solution state, it is expected that there will be no phosphorescence (Fig. 1d). But
- ⁵⁰ in crystalline state due to 'directed' heavy atom effect, there is significantly close proximity between the aromatic carbonyl and bromine which leads to the partial delocalization of electrons of carbonyl oxygen to bromine (Fig. 1e and 1f). Moreover, in crystalline state the nonradiative relaxation from
- 55 the triplet state due to the thermal vibration is reduced as the atoms are relatively fixed in crystal lattice positions. These facts synergistically enhanced the triplet sate population and radiation from there in crystalline state. The differences in the photoluminescence properties of the crystals obtained from
- 60 ethyl acetate and methanol can be attributed by the effect of crystallization conditions and crystal packing. Emission spectra of foldamer 2 in glassy solutions (77 K) exhibit no additional peak in the 460-500 nm. The foldamer 1 shows no significant luminescence (ESI Fig. 4) in solid state.

X-ray crystallography[±] shed some light on this fact at atomic level. Foldamer 1 containing two molecules in the asymmetric unit and there is no intramolecular hydrogen bond. In higher order, foldamer 1 formed an antiparallel hydrogen bonded dimer in the solid state (Fig. 2a). Foldamer 70 2 crystallizes with one molecule in the asymmetric unit from both ethyl acetate and methanol solution (ESI Fig. 5). There exist a six member intramolecular hydrogen bond. Two molecules of the foldamer 2 form antiparallel duplex by reciprocal intermolecular hydrogen bonding interactions 75 between maba NH and urea C=O (Fig. 2b). In higher order assembly each duplex is linked to four other duplexes via halogen bonding between maba C=O and bromine atom (C7=O3....Br1, 3.15Å, 4.31Å, 159° from methanol, N3-H3....O4, 3.29Å, 4.43Å, 159° from ethyl acetate) and thereby 80 forms a two dimensional layer like structure along the crystallographic b direction (ESI Fig. 6). Hence, due to the closer proximity between the carbonyl oxygen and bromine (3.15 Å) in the crystals from the methanol solution, they should show stronger phosphorescence compared to that ss obtained from ethyl acetate (3.29 Å) (Fig. 2c and 2d). Hydrogen bonding parameters are listed in Table 1.



Fig. 2 The antiparallel duplex by (a) foldamer **1** and (b) foldamer **2**. The C=O....Br bond in foldamer **2** crystal from (c) ethyl acetate and (d) methanol solution. Cyclohexyl groups here appear as purple ¹¹⁰ spheres and *t*-butyl groups as pink spheres.

Foldamer	D-HA	HA(Å)	DA(Å)	D-HA (°)
1	N3-H3O4c	2.12	2.97(7)	172
	N6-H6O8k	2.05	2.89(7)	167
2, EtOAC	N3-H304e	2.23	3.05(6)	163
	N2-H5O3	2.02	2.64(6)	128
2, MeOH	N1-H104e'	2.19	3.02(3)	162
	N3-H3O3	2.06	2.65(4)	125
^a Symmetry equivalent c = 2-x, -y, 1-z ; k = -x, 1-y, -z ; e = 1-x, -y, -z ; e' = 1-x, 2-y, 2-z.				

¹¹⁵ The photoluminescence lifetime of foldamer **2** in chloroform solution and in crystals obtained from ethyl acetate and methanol

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were measured. For all three cases, the excitation wavelength was 290 nm and the emission was acquired at 467 nm. The crystals were gently crushed in a mortar pestle and put into the groove of the solid sample probe for lifetime measurements. The data 5 obtained were well fitted with the single exponential decay model. The results show that in chloroform solution the lifetime of the compound is in nanosecond regime (4 ns) (ESI Fig. 7) responsible for fluorescence. Whereas the lifetime of the compound in crystals obtained from ethyl acetate solution is in 10 microsecond regime (11 µs) which corresponds to phosphorescence (Fig. 3a). Fig. 3a inset shows the green phosphorescence as evident from the photographs under 254 nm UV light. The crystal obtained from methanol solution exhibits increased phosphorescence lifetime (13 µs) compared to the 15 crystals from ethyl acetate (Fig. 3b). Fig. 3b inset shows the

strong green phosphorescence under 254 nm UV.



Fig. 3 The time resolved decay curves of the crystals obtained from (a) ethyl acetate and (b) methanol solution. Insets, the photographs of the respective crystals under laboratory light and 254 nm UV light.

- ⁵⁰ In summary, we have shown the phosphorescence from purely organic compounds in solid state at normal condition. The increase in phosphorescence lifetime and intensity significantly depends on the extent of halogen bonding interaction where distance between the carbonyl oxygen and ⁵⁵ the bromine atom plays an important role to the triplet state
- population and emission. The results provide atomic level insights over the halogen bonding and phosphorescence.

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Notes and references

[‡] Crystallographic data: Foldamer **2** from EtOAc: C₂₅H₃₆BrN₃O₄, M_w = 522.47, monoclinic, space group *P21/c*, *a* = 13.649(13), *b* = 16.921(16), *c* = 12.008(12) Å, α = 90°, β = 108.526(15)°, γ = 90°V = 2629(4) Å³, Z = 4, 65 d_c = 1.320 Mgm⁻³, T = 100 K, $R_1 = 0.0526$ and $wR_2 = 0.1191$ for 4442 data with $I > 2\sigma(I)$. From MeOH: C₂₅H₃₆BrN₃O₄, $M_w = 522.48$, monoclinic, space group *P21/c*, *a* = 13.479(19), *b* = 16.843(2), *c* = 1.0076(2002) 0.0000 (2002) 0.0000 (2000) 0.00000 (2000) (20000) 0.00

- 11.834(17) Å, $\alpha = 90^{\circ}$, $\beta = 107.838(2)^{\circ}$, $\gamma = 90^{\circ}$ V = 2557.5(6) Å³, Z = 4, $d_{\rm c} = 1.357$ Mgm⁻³, T = 100 K, $R_1 = 0.0364$ and $wR_2 = 0.0914$ for 4450 70 data with $I > 2\sigma(I)$. Intensity data were collected with MoK α radiation for foldamer **2** at 100 K using Bruker APEX-2 CCD diffractometer. Data were processed using the Bruker SAINT package and the structure solution and refinement procedures were performed using SHELX97.¹⁴ For foldamer **2** non-hydrogen atoms were refined with anisotropic
- 75 thermal parameters. The data for foldamer 2 from EtOAc and MeOH have been deposited at the CCDC with reference number CCDC 942338-942337 respectively.
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