Self-assembly characteristics of a multipolar donor-acceptor-based bis-pyrene integrated molecular tweezer

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Abstract. A modular design of a molecular tweezer is presented that integrates a multipolar D- π -A [D: Donor, A: Acceptor] scaffold, 1-aminopyrene-based fluorophore units and L-alanine-based linkers. The synthesis of the molecule is based on two-fold aromatic nucleophilic reactions (ArS_N) and coupling reactions of the acid and amino functionalities. This molecule crystallizes in a non-centrosymmetric (P21) space group. We present its rich self-assembly characteristics that involves an array of π -stacking interactions. In addition, the molecular tweezer within its cleft forms H-bonding with two dimethylformamide molecules. Such multipolar D- π -A systems containing chiral and fluorophore units are potential candidates for a number of electronic and photonic applications.

Keywords. Amino-pyrene; π -conjugated systems; supramolecular self-assembly; molecular electronics; fluorescent probes and chemosensors.

1. Introduction

In search of smart molecular electronic devices, π -conjugated systems have drawn special attention. These have been applied as building blocks to develop new classes of multi-responsive electronic materials. Supramolecular self-assembly of planar π -conjugated systems^{1a} represent one of the most frequently applied design strategies for construction of functional organic nano-devices.^{1b}

In this context, pyrene derived molecular systems are of major interest towards designing organic electronic devices, for example, sensors, dye sensitized solar cells, light emitting diodes, semiconductors, etc.^{2,3} Pyrene moiety has also been integrated with a variety of molecular scaffolds to generate nano-architectures like supramolecular capsules, emissive nanofibers, nanotubes, etc.⁴ In addition to their electronic properties, pyrene-based materials find applications in a number of biological processes such as in cell imaging, structural study of proteins, peptides, lipid membranes, temperature sensors, etc.⁵ Most of these properties rely on weak supramolecular interactions and their diverse packing modes. More specifically, 1-aminopyrene and its electronic properties, photophysical properties, excitation

dynamics, light harvesting, etc.,⁶ has been the topic of recent interest.

In our group, we have been interested in designing molecular systems that can utilize D-A based interactions to undergo selective electron transfer (ET) reactions and produce paramagnetic radical ion probes.⁷ Also, we have shown that supramolecular interactions can be used to modulate non-linear optical (NLO)⁸ and ferroelectric properties⁹ of D- π -A-based molecules. The π - π stacking interactions play an important role in determining the effective properties of these materials.

Herein, we have designed a molecular tweezer that integrates a multipolar D- π -A building block, two aminopyrene-based fluorophore units and two L-alanine-based linkers (scheme 1). The synthesis of the molecule was based on two-fold aromatic nucleophilic reactions (ArS_N) and coupling reaction of the acid and amino functionalities. We present its rich self-assembly characteristics¹⁰ that exhibits three-dimensional network formation through π - π stacking interactions and its trapping of dimethylformamide molecules.

In essence, the molecule constitutes a multipolar D- π -A unit, H-bonding encapsulating units, chiral units and fluorophore units. This should make the molecule and the self-assembled structure multi-responsive to a variety of stimulus.

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Scheme 1. Scheme showing modular design of 1.

2. Experimental

2.1 Materials and physical measurements

Chemicals 1-aminopyrene, 1,5-difluoro-2,4-dinitro benzene and L-alanine were obtained from Sigma Aldrich and were used as received. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator having particle size of 25 μ m and was sourced from Merck India. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer in $\text{DMSO-}d_6$ with TMS as standard. Infra-Red spectra were recorded in KBr pellet using Varian 3100 FT-IR instrument. MALDI-TOF mass spectral data was obtained using a Bruker made Autoflex TOF/TOF instrument and α -Cyano-4-hydroxycinnamic acid as the matrix. Infra-Red spectrum was recorded in KBr pellets using a Varian 7000 FT-IR instrument. The UV-vis absorption spectrum was taken in dichloromethane (DCM) solvent using a JASCO V-600 model spectrometer. The steady state fluorescence spectrum was measured in DCM using a Varian Cary Eclipse Fluorescence Spectrometer.

2.2 Design and synthesis

Our molecular design utilizes a 1,5-difluoro-2,4-dinitro benzene as the precursor unit in order to integrate the two aminopyrene groups with the L-alanine spacers (scheme 1). Compound 1 was synthesized in two simple steps and was fully characterized by various analytical techniques such as mass, NMR and IR spectroscopy (Supplementary Information). The starting material bis-alanine functionalized derivative of 1,5-difluoro-2,4-dinitro benzene (**1a**) was obtained by following a previously reported method,¹¹ which was then further reacted with 1-aminopyrene in dichloromethane in the presence of *N,N*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP) and hydroxybenzotriazole (HOBt) under reflux conditions (scheme 2). To obtain molecule **1a**, reagents 1,5-difluoro-2,4-dinitro benzene (0.75 g, 3.7 mmol), L-alanine (0.65 g, 7.3 mmol) and sodium carbonate (0.78 g, 7.4 mmol) were mixed

in a 100 mL round bottomed flask containing 30 mL of 50% EtOH. The mixture was stirred and then initially heated upto 50°C for 30 minutes and then at 60°C for next 10 minutes. Reaction mixture was then cooled down to 10°C. Solvent was evaporated using rotary evaporator and obtained solid was washed with EtOH. The residue was neutralized with 5N HCl to yield 850 mg of **1a**. In the next step molecule **1a** (0.26 g, 0.7 mmol) was taken with DMAP (0.66 g, 3.2 mmol) in 30 mL of dry dichloromethane and stirred for 15 minutes under inert atmosphere at 0°C. To the stirred mixture 1-aminopyrene (0.4 g, 1.8 mmol) was added followed by the subsequent addition of DCC (0.66 g, 3.2 mmol) and HOBt (0.26 g, 1.7 mmol) into the ice cooled reaction mixture and continued the stirring for 15 h with gradual heating up to room temperature. The crude product was purified by performing column chromatography. ^1H -NMR ($\text{DMSO-}d_6$, 294K, ppm): δ 10.41 (2H, PyNHCO), 9.12 (s, 1H, dinitrobenzene CH), 9.08–9.05 (2H), 8.33–8.09 (18H, PyCH), 6.06 (1H, dinitrobenzene CH), 4.81 (2H, CH_3CH), 1.80 (6H, CH_3). ^{13}C -NMR ($\text{DMSO-}d_6$, 294K, ppm): δ 171.8, 147.4, 131.2, 131.1, 130.9, 130.8, 129.4, 129.2, 128.8, 127.9, 127.7, 127.5, 127.0, 126.0, 125.7, 125.5, 125.3, 124.8, 124.7, 124.6, 124.2, 122.6, 115.7, 115.6, 92.5, 53.2, 19.0. MALDITOF mass (*m/z*) calculated $\text{C}_{44}\text{H}_{32}\text{N}_6\text{O}_6$: 740.8, found 740.9.

2.3 X-ray crystallography

X-ray quality crystals of molecule **1** were grown from DMF/ CHCl_3 (1:1.3) solvent mixture by slow evaporation method at room temperature. The reported data set was collected by mounting the crystal with paratone oil at 100 K, on a Bruker's Apex-II CCD diffractometer using Mo $\text{K}\alpha$ ($\lambda = 0.71069 \text{ \AA}$). The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using 01SADABS from Bruker. The number of total, independent and observed reflections ($[I > 2\sigma(I)]$ for theta 25°) were 24405, 11089, 7544. The structures were solved by direct methods using SIR-92 and refined by full-matrix least squares refinement methods based on F^2 , using SHELX-97.

3. Results and Discussions

3.1 Optical properties

Absorption and emission properties are of major importance while designing materials for sensing, photonic and light harvesting applications.¹² Pyrene moiety is

Scheme 2. Synthetic steps and conditions for preparation of **1**.

known for its high quantum yield and excimer emission properties and therefore pyrene derivatives represent a class of materials with exciting optical properties.¹³

Dichloromethane solution of molecule **1** shows absorption around 345 nm and a shoulder peak at 400 nm (figure 1). Emission spectrum of molecule **1** (figure 1, blue spectrum) in dichloromethane solvent shows typical emission between 370–520 nm with major intensity at 410 nm.

However, if pyrene moiety in excited state is close to ground state pyrene ring (~ 10 Å) the interaction between such pairs can result in excimer emission.^{13a,14}

3.2 Crystal structure

Molecule **1** crystallizes into a monoclinic system with a non-centrosymmetric space group $P2_1$, which falls in one of the ten polar point groups (table 1).

Figure 1. Absorption and emission spectrum of molecule **1** in dichloromethane.

Crystallization in a polar point group is a necessary condition for applications such as ferroelectricity and related properties like piezoelectricity, pyroelectricity and non-linear optical activity.¹⁵ Single crystal X-ray data reveals a unit cell containing two molecules in each unit (figure S2). The two pyrene groups in the molecule are expanded in space to impart a ‘V-type structure’ (figure 2). This excludes the possibilities of formation of molecular clip type arrangement in which two pyrene groups face each other.

Two *N,N'*-dimethylformamide (DMF) solvent molecules (figure S1 & S2) form intermolecular hydrogen bonds (H-bonds) with two pyrene N-H groups (figure 2). The H-bonding parameters are dissimilar. The O—H distances are 1.99 Å and 2.20 Å respectively, whereas, O—N distances are 2.85 Å and 3.02 Å and N—H—O angles are at 172.4° and 160.3° respectively. This suggests one DMF molecule to be bound more tightly than the other.

Figure 2. Hydrogen bonding pattern with the two DMF molecules. H-atoms which are involved in hydrogen bonding are shown for clarity.

Table 1. Crystal data of **1**

Empirical formula	C ₅₀ H ₄₆ N ₈ O ₈
Formula weight	886.95
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	a = 13.3490(8) Å, α = 90° b = 11.6327(7) Å, β = 93° c = 13.7654(6) Å, γ = 90°
Volume	2134.4 Å ³
Z	2
Density calculated	1.380 Mg/m ³
Absorption coefficient	0.096 mm ⁻¹
F(000)	932
Crystal Size	0.28 × 0.20 × 0.14 mm ³
Theta range for data collection	1.48 to 29.46°
Reflections collected	24405
Independent reflections	11089 [R(int)=0.065]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	11089/1/633
Goodness-of-fit on F ²	0.901
Final R indices[I > sigma(I)]	R1 = 0.0593, wR2 = 0.1318
R indices (all data)	R1 = 0.0982, wR2 = 0.1584
Absolute structure parameter	−0.6(11)
Largest diff. peak & hole	0.304 and −0.243 eÅ ⁻³
CCDC	996279

Figure 3. Ortep (POV-ray) diagrams (a & b) showing π - π stacks leading to a 1-dimensional molecular chain formation along the b-axis.

3.3 Supramolecular network

The single-crystal structure shows formation of extended supramolecular chains through stacking interactions between the diamino- dinitrobenzene and the electron rich pyrene units (figure 3). There is no H-bonding interaction along the molecular chain (b-axis) and therefore π - π stacking interactions play crucial role in the network formation.

Molecules pack in such a way that diamino-dinitrobenzene of one molecule faces the pyrene group of other and so on (figure 3a-b). As shown in figure 3b the 1,5-dinitrobenzene moiety is sandwiched between two pyrene groups from different molecules in the chain. Centroid-centroid distance between two stacked pyrene-dinitrobenzene moieties is 3.90 Å and 7.74 Å (figure 3a). As the molecule **1** is a rigid system, the

central molecule adjusts its orientation in a way to facilitate stacking interactions (shown in green circle). This arrangement finally leads to formation of a supramolecular molecular chain. These one dimensional molecular chains further pack along a-axis to form a 2-dimensional network (figure 4a). These structures form 3-dimensional network as shown in figure 4b. As can be seen, dinitrobenzene rings are sandwiched between aminopyrene rings and come exactly over one-another resulting in a nicely packed arrangement of pyrene rings.

We anticipate that the strict compliance of the symmetry constraints by this modular molecule i.e., its favourable polar arrangement would be highly significant for its futuristic applications as NLO and ferroelectric materials.¹⁶ Furthermore, the integrated multiple units would bestow a high degree of stimuli responsiveness.¹⁷

Figure 4. (a) POV-ray diagram of two-dimensional network and (b) three dimensional self-assembly of molecule.

4. Conclusions

We have designed and synthesized a modular molecule which constitutes a multipolar D- π -A unit, H-bonding groups, encapsulating unit, chiral centres and fluorophore units. The molecule crystallizes in one of the ten polar point groups satisfying the symmetry prerequisites for a number of important material properties such as NLO, ferroelectricity, piezoelectricity, etc. We have demonstrated the supramolecular self-assembly characteristics of this molecule in the solid state.

Supplementary Information

The detailed procedure for synthesis and characterization, MALDITOF Mass, IR, ^1H and ^{13}C , DEPT-135, APT NMR spectra, X-ray crystallographic tables are given in SI file available at www.ias.ac.in/chemsci.

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