

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-A (Donor, 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 (A15) 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-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; Fluorescent probes and chemosensors molecular electronics;

1 Introduction

In search of smart molecular electronic devices, 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 represent one of the most frequently applied design strategies for construction of functional organic devices.

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. Pyrene moiety has also been integrated with a variety of molecular scaffolds to generate nano-architectures like supramolecular capsules, emissive nanofibers, nanotubes, etc. 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. 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. 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 Also, we have shown that supramolecular interactions can be used to modulate non-linear optical (NLO) and ferroelectric properties of D--A-based molecules The 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--A building block, Two aminopyrene-based fluorophore units and two L- alanine-based linkers (scheme 11. The synthesis of the molecule was based on two-fold aromatic nucleophilic reactions (ArS) and coupling reaction of the acid and amino functionalities. We present its rich self-assembly characteristics" that exhibits three- dimensional network formation through - stack- ing interactions and its trapping of dimethylformamide molecules.

In essence, the molecule constitutes a multipolar D 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 stiumulus

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Scheme 1.

Scheme showing modular design of 1.

2. Experimental

21 Materials and physical measurements

Chemicals 1-aminopyrene, 1,5-difluor-2,4-dinitro ben- zene and L-alanine were obtained from Sigma Aldrich and were used as received. Thin layer chromatogra phy (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator hav- ing particle size of 25 m and was sourced from Merck India. ¹H and ¹³C NMR spectra were recorded on a Bruker 500 MHz spectrometer in DMSO-d₆ with TMS a 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 a-Cyano--hydroxycinnamic acid as the matrix Infra Red spectrum was recorded in KBr pellets using a Varian 7000 FT-IR instrument. The UV - vin absorp tion 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 I 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 previ- ously reported method," which was then further reacted with 1-aminopyrene in dichloromethane in the pres- ence of N, N -dicyclohexylcarbodiimide (DCC), 4- (dimethylamino)pyridine (DMAP) and

hydroxybenzo triazole (HOBt) under reflux conditions (scheme 2). To obtain molecule Ia. 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 30mL 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 Ia. In the next step molecule Ia (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 (DMSO-d₆, 294K, ppm) & 1041 (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, C*H₂*C*H₂) 1.80 (6H C*H₃) ¹³C-NMR (DMSO-d₆, 294K, ppm) & 171.4, 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 CuHNO: 740.8, found 740.9.

23 X-ray crystallography

X-ray quality crystals of molecule I were grown from DMF/CHCl₃ (11:3) solvent mixture by slow evaporation method at room temperature. The reported data set was collected by mounting the crystal with paratone dil at 100 K, on a Bruker's Apex-II CCD diffractometer using Mo K α ($\lambda=0.71069$ Å). The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. The number of total, independent and observed reflections ($I > 2\sigma(I)$ for $\theta > 25^\circ$) 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_o , 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." Pyrene moiety is

$x^2 - 3x - 5a^2$
donor-acceptor

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NH

OH

Na₂CO₃, 50% EIGH

HN

O₂*S

HN

NH

ON

O₂ * M²

DCC DMAP

HOBt DCM Reflux

Synthetic steps and conditions for preparation of 1

K₂O₂

Scheme 2.

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 ($\overset{-10}{\text{A}}$) the interaction between such pairs can result in excimer emission 114

32 Crystal structure

Molecule 1 crystallizes into a monoclinic system with a non-centrosymmetric space group P2₁ which fills in one of the ten polar point groups (table 1).

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 OH distances are 1.99 Å and 2.20 Å respectively,

whereas, O-N distances are 2.85 Å and 3.02 Å and NH - O angles are at 172.4 and 160.3 respectively. This suggests one DMF molecule to be bound more tightly than the other.

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Emission Absorption

15

250

300

350

400

450

Wavelength (nm)

500

850

600

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

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

(a)

Table 1. Crystal data of 1

Empirical formula

7.7 Å

Formula weight

Temperature

Wavelength

Crystal system

Space group

Unit cell

dimensions

Co Has No O

886.95

1002) K

071073 A

Monoclinic

P21

21344 A $\gamma = 90$ deg

2

$x = 13.349(8) * \lambda$

$a = 90$ deg

$b = 11.6327(7) * A$

$\beta = 93$ deg $c = 13.7654(6) * \lambda$

1.38Mg / (m [^] 2)

(b)

Volume

Density calculated

Absorption coefficient

F(000)

Crystal Size

Theta range for

data collection

Reflections collected

Independent

reflections

Refinement method

0.096 mm

932

028 * 0.2 * 0

mm

1.48 to 29.46 24405

11089

[Rint]=0.065] Full matrix least-squares

on F

Data/restraints/parameters Goodness-of-fit on F

Final R

indices[1-sigma(E)] R indices (all data)

Absolute structure

parameter

Largest diff. peak & hole

11089/1/633

0.901

RI = 0.0593

WR2 = 0.1318 RI = 0.09/2

-0.6(11) * R * 2 = 0 .

0.304 and -0.243 e λ) 996279

= 0.1584

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

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 alternating in a nicely packed arrangement of pyrene rings nopyrene rings and come exactly over one-another re-

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 $\pi^*\pi$ 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

symmetry constraints by this modular molecule its favourable polar arrangement would be highly We anticipate that the strict compliance of the significant for its futuristic applications as NLO and ferroelectric materials, 1 Furthermore, the integrated multiple units would bestow a high degree of stimuli responsiveness 17

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(b)

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--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 ¹³C. DEPT-135. APT NMR spectra, X-ray crystallographic tables are D. given in SI file available at www.jas.ac.in/chemsci

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