INTERPLAY OF MONOMER-EXCIMER EMISSION IN ATHRACENE-IMIDAZOLIUM CONJUGATES

In partial fulfillment for the award of the degree of

MASTER OF SCIENCE IN CHEMISTRY

By

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DECLARATION

*I hereby declare that the project report entitled "**Interplay of Monomer-Excimer Emission in Anthracene-Imidazolium Conjugates"** is a bonafide record of the work carried out by me under the guidance of **Dr. Nandajan P. C.** at MES College Nedumkandam, in partial fulfillment of the Degree of Master of Science in Chemistry (Pure Chemistry), Pavanatma College Murickassery, Idukki, Kerala.*

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CERTIFICATE

*This is to certify that Ms. SNEHA ANTONY has worked on "**Interplay of Monomer-Excimer Emission in Anthracene-Imidazolium Conjugates"** under my guidance at MES College Nedumkandam in partial fulfillment of the Degree of Master of Science in Chemistry Pavanatma College Murickassery, Idukki, Kerala.*

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CERTIFICATE

This is to certify that ***Ms. Sneha Antony*** *has worked on "****Interplay of Monomer-Excimer Emission in Anthracene-Imidazolium Conjugates"*** *under the supervision of Dr. Nandajan P. C. at MES College Nedumkandam, in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry, Pavanatma College Murickassery, Idukki, Kerala.*

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SNEHA ANTONY

CONTENTS

1. ABSTRACT

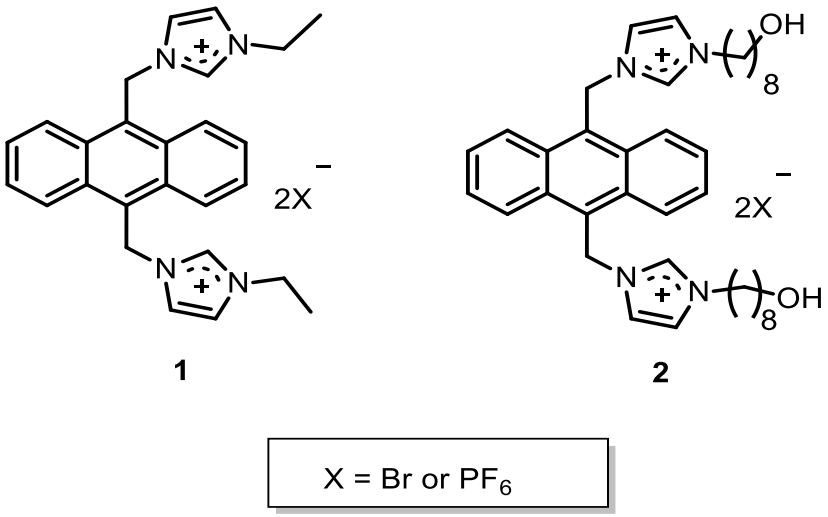
We designed, synthesised and investigated photophysical properties of anthracene-imidazole conjugates in organic, aqueous and solid media. These systems were synthesised in moderate to good yields and exhibited characteristic anthracene absorption (350-425 nm) and emission (400-525 nm) behaviour in the organic and aqueous media. In the solid state, molecule **1** exhibited anthracene monomer emission at 422 nm, while both excimer and monomer emission were observed for the molecule **2** having pendant hydroxyl groups. Additional information regarding the fluorescence properties of these systems were obtained by studying the molecular packing of **2** through single crystal X-ray structure analysis. The crystal structure analysis of the molecule **2** showed a unidirectional packing, in which its excimer emission was reasoned as edge-to-edge type interactions. Hence, careful selection of the pendant groups allows us to fine-tune the photophysics of the molecules and which in turn results in the development of the tailor-made materials for opto-electronic applications.

2. INTRODUCTION

Development of organic molecule based photonic devices becomes an exciting area of research in the past few decades (Bonifazi *et al.*, 2012; Jenekhe *et al*., 2011; Hiyama *et al.*, 2010; Li *et al.*, 2010; Scherf *et al.*, 2006). Majority of the available organo-photonic materials exhibit excellent optoelectronic properties in dilute solutions. However, in concentrated solutions and in the solid state these fluorophores undergo aggregation, which results in the loss of the favorable properties (Tang *et al.*, 2011; 2009; Swager *et al.*, 2007). In this perspective, a few successful approaches have been projected in which covalent attachment of branched chains or bulky groups such as dendrimers to the fluorophore core retards the aggregation process (Tang *et al*., 2011; Balzani *et al.,* 2008). Other endeavors used to prevent the aggregation include the doping of the fluorophore on a polymer matrix or by encapsulation in a bulky host molecule (Galoppini *et al.*, 2012; Smith *et al.*, 2009; Swager *et al.*, 2007). In a technological point of view, if these adaptations require extensive experimental protocols, then the final outcome would be less lucrative. Therefore, the real challenge faced by a material chemist is to design a simple molecular system that warrants favourable properties as well as cost-effective mass production.

Anthracene derivatives emerged as a promising candidate as a building block for Organic Light Emitting Diodes (OLEDs) after the invention of electroluminescence from crystals of anthracene in 1960s (chen *et al.*, 2009. Presence of intrinsic planarity and grid structure in anthracene limits its use as it causes fluorescence concentration quenching and emission wavelength bathochromic shift in the solid state. Successful attempts for electroluminescence from anthracene derivatives were achieved by various groups among which one of the first report by Adachi et al. shows a luminescence of 0.09 cd m^{-2} at 100 Ma cm^{-2} (M. Zhu *et al.*, 2013). Although they could achieve electroluminesce from anthracene derivatives, the lower device efficiency were identified as due to easy crystallisation in the

solid-state thin film. This lower efficiency was further solved by synthesizing materials with twisted donor-acceptor (D-A) structures(M.-G.Shin *et al*., 2012). In this context, we report the synthesis, photophysical properties and structure-proerty relationship of molecules **1** and **2** (Chart 1.1).



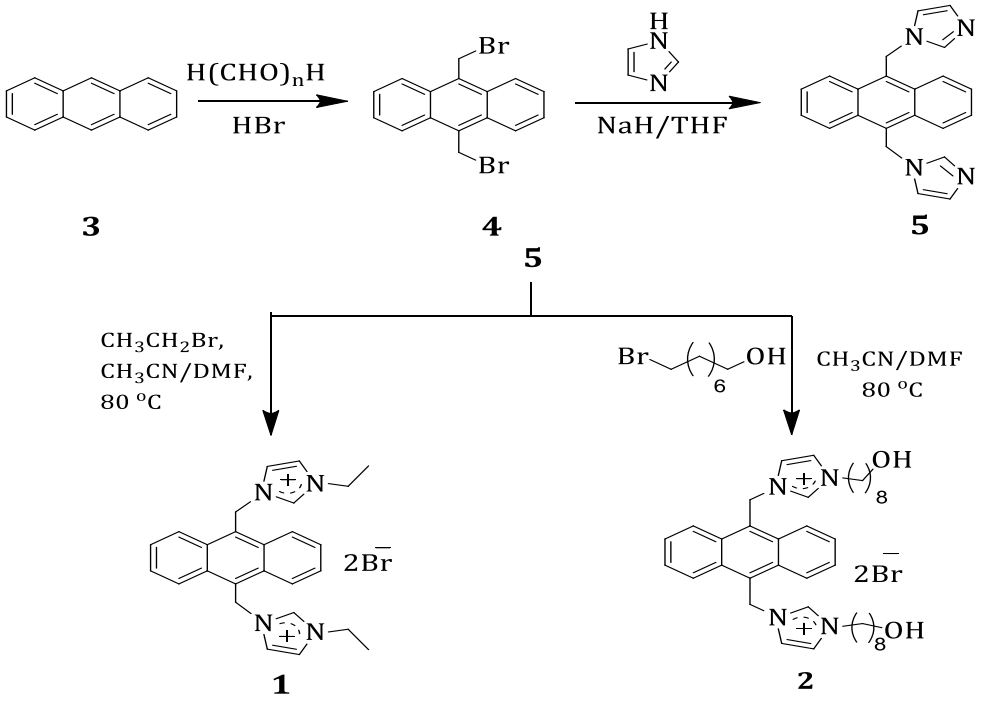
1 **2**

chart 1.1

3. RESULTS AND DISCUSSION

3.1. SYNTHESIS

Synthesis of the imidazole based compounds 1 and 2 were carried out as shown in scheme 1.1. Bromomethylation of anthracene using HBr in glacial acetic acid resulted in the 9,10-bis(bromomethyl)anthracene (**4**) in 95% yield. The reaction of **4** with imidazole in the presence of NaH in THF yielded 78% of 9,10-bis((1H-imidazol-1-yl)methyl)anthracene (**5**). The subsequent reaction of **5** with bromoethane results in compound **1** in quantitative yield. While the reaction of **5** with 8-bromooctanol resulted in the compound **2** in 61% yield. All these compounds were characterized on the basis of spectral data and analytical results.



Scheme 1.1. Synthesis of the compounds **1** and **2.**

3.2. UV-VIS AND FLUORESCENCE PROPERTIES IN SOLUTION

The absorption properties of these compounds were studied in organic and aqueous medium. Figure 1.1 shows the absorption spectra of the compounds in methanol. These systems showed characteristic anthracene absorption spectra with vibrational fine structures in between 370-400 nm. For example, compound **1** exhibited an absorption maximum at 396 nm. The absorption characteristics of all the derivatives in aqueous medium were found to be similar to that observed in methanol (Figure 1.2).They also exhibit characteristic anthracene fluorescence behavior in methanol as emission maxima in the region 418-430 nm (Figure 1.3) and in aqueous solutions as in between 390-500 nm (Figure 1.4). photophysical properties of these derivatives in solution were summarized in the table 1.1.

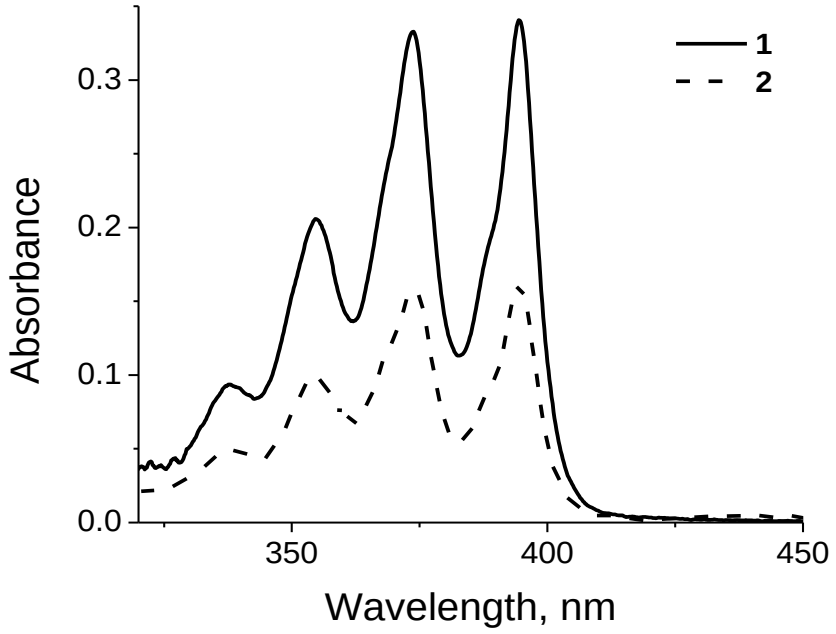


Figure 1.1. Absorption spectra of the **1** (12μM) and **2** (8μM) in methanol.

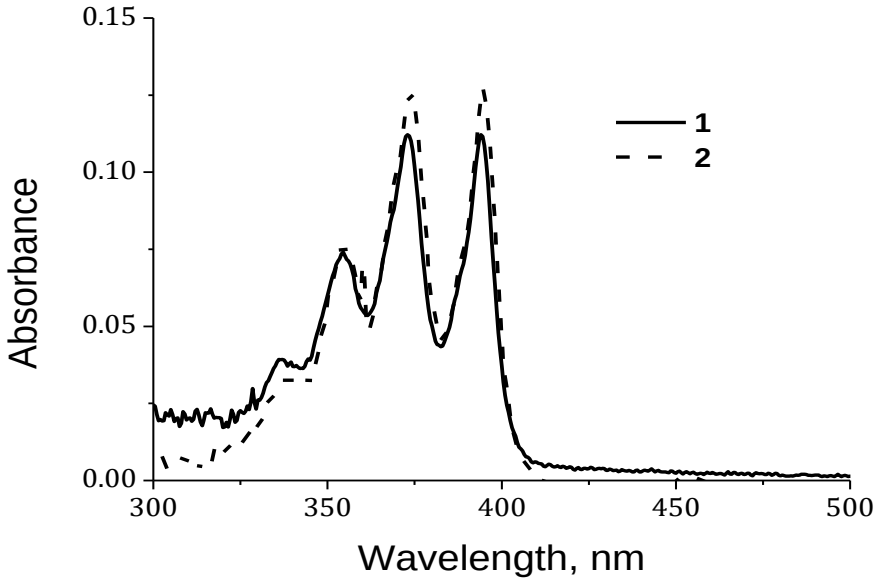


Figure 1.2. Absorption spectra of **1** (10 μM) and **2** (8 μM) in aqueous medium.

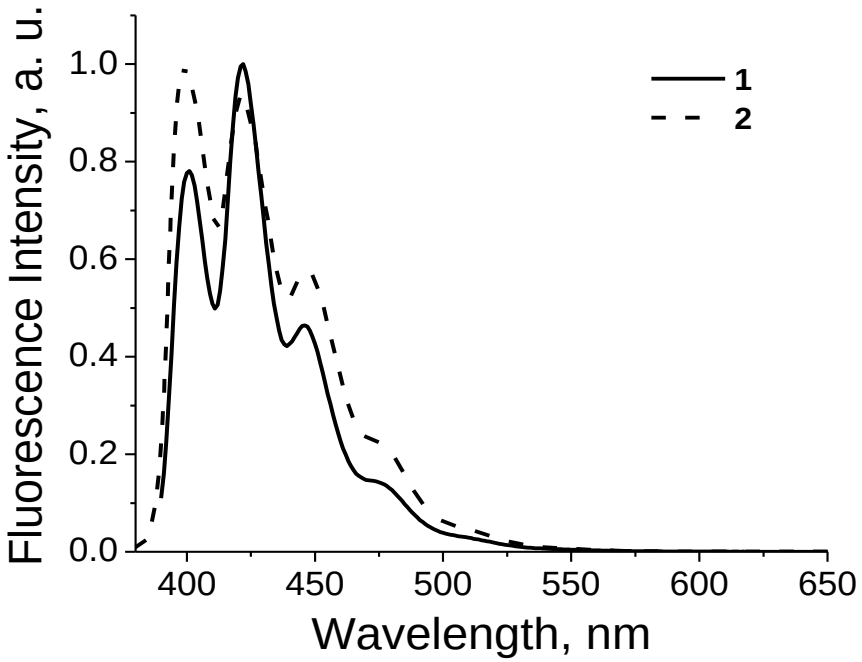


Figure 1.3. Normalized fluorescence spectra of **1** and **2** in methanol. Excitation wavelength, 355 nm.

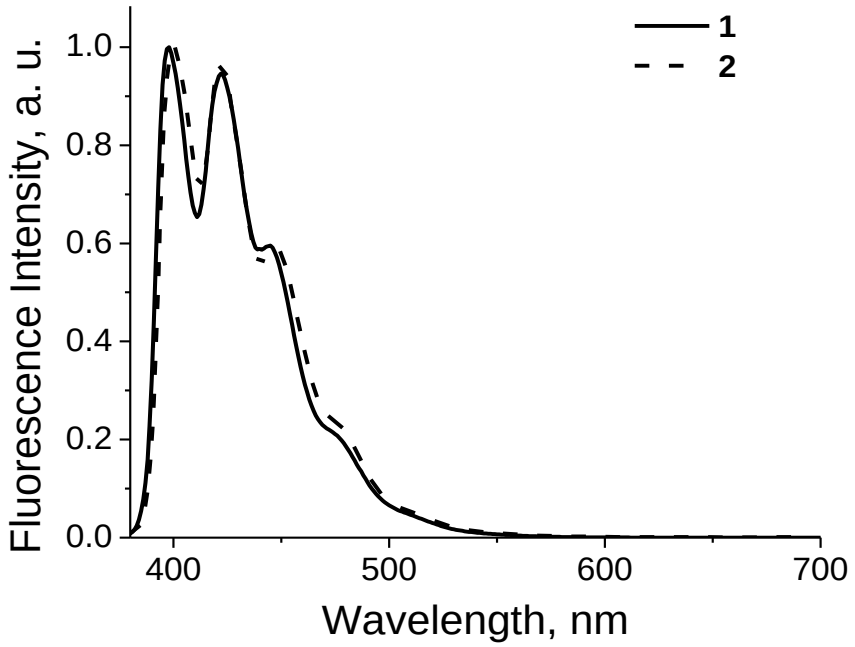


Figure 1.4. Normalized fluorescence spectra of **1** and **2** in water. Excitation wavelength, 355 nm.

Table 1.1. Summary of the photophysical properties of the compounds in solution

	λ_{abs} (nm) (Methanol)	λ_{abs} (nm) (water)	λ_{em} (nm) (Methanol)	λ_{em} (nm) (water)	Φ_F (methanol)	Φ_F (water)
1	394	394	422	398	0.58	0.62
2	395	395	399	400	0.63	0.61

3.3. UV-VIS AND FLUORESCENCE PROPERTIES IN THE SOLID STATE

The development of photonic devices based on organic molecules has been an exciting area of research in the past few decades (Bonifazi *et al.*, 2012; Jenekhe *et al*., 2011; Hiyama *et al.*, 2010; Li *et al.*, 2010; Scherf *et al.*, 2006). In this regard, it was of our interest to investigate the photophysical properties of these compounds in solid state because such efficient molecules can have potential applications in device fabrication (Scherf *et al.*, 2006;). In this context, we investigated the solid state photophysical properties of these molecules in the powdered state. The reflectance spectra of the molecules 1 and 2 in the powdered state are shown in Figure 1.5. As compared to the solution, the absorption spectra of all the derivatives in the solid state were significantly broad and red-shifted with maxima in the region between 375-410 nm. The absorption spectra of the molecules 1 and 2 showed a λ_{max} of 395 and 398 nm correspondingly. Figure 1.6 shows the fluorescence spectra of compound 1 and 2 in the solid state. The compound 1 displayed an emission maximum at 422 nm along with a shoulder around 500 nm with blue fluorescence in the solid state. While the emission spectrum of compound 2 consisted of an emission maximum at 528 nm along with a band at 427 nm. The fluorescence quantum yields of the molecules 1 and 2 in solid state was found to be 10% and 8% respectively.

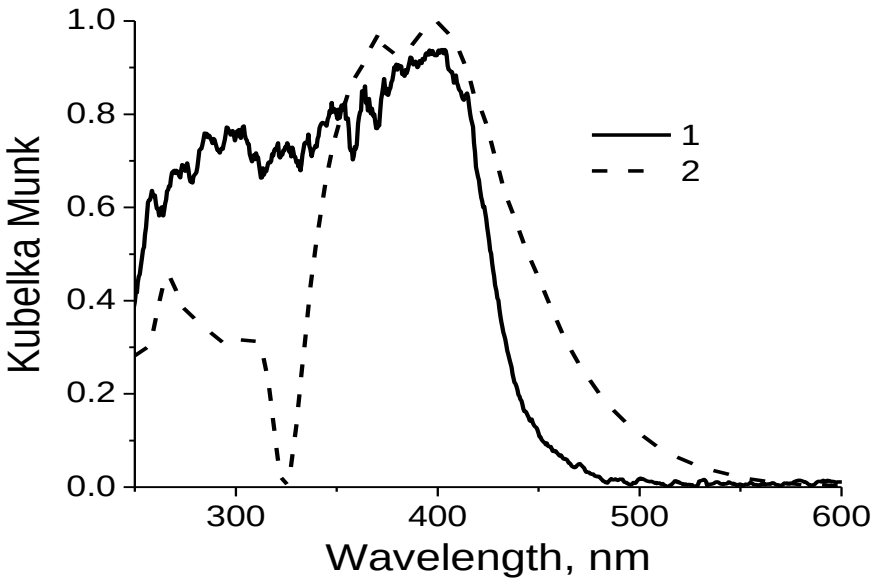


Figure 1.5. Absorption spectra (obtained by transforming the reflectance spectra) of **1**, **2** in the solid state.

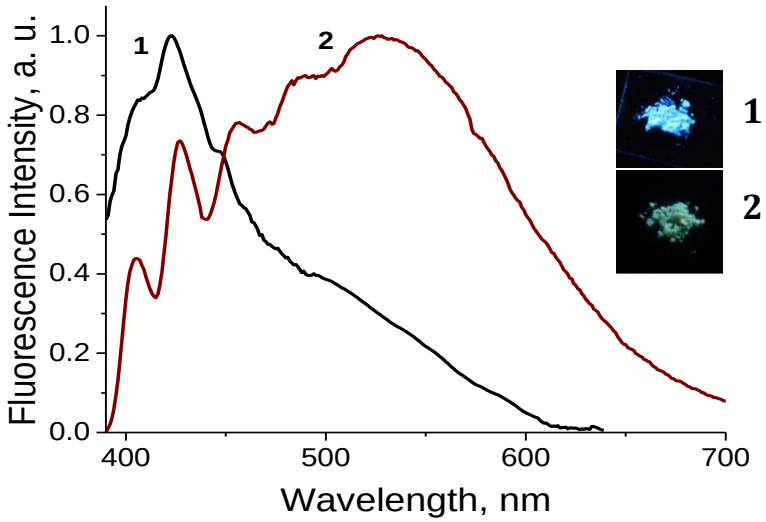


Figure 1.6. Normalized fluorescence spectra of the molecules **1** and **2** in the solid state. λ_{ex}, 355 nm. Inset shows the visual fluorescence of the molecules **1** (blue, top), and **2** (yellow, bottom) when excited with a hand-held UV lamp. Excitation wavelength, 365 nm.

3.4. CRYSTAL STRUCTURE ANALYSIS

In the solid state, the molecule **2** under study exhibited emission in the longer wavelength region though their emission maxima and intensities varied significantly. The differences in the solid state photophysical properties were revealed from the single crystal X-ray structure data. The crystal of the molecule **2** was obtained from 4:1 mixture of methanol and hexane. Figure 1.7 shows the crystal structure of the molecule **2** and table 1.2 summarizes their crystal data.

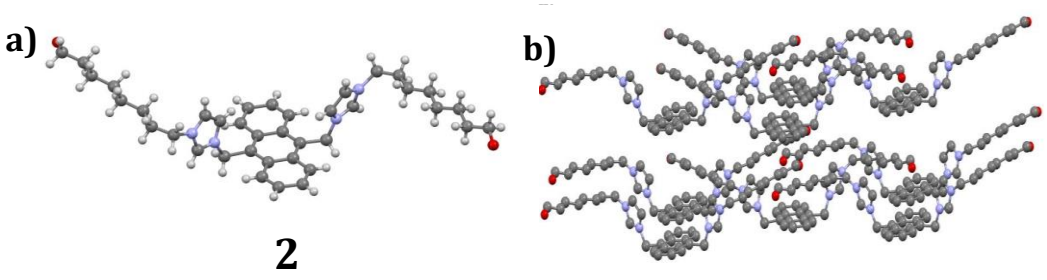


Figure 1.7. a) Single crystal X-ray structure of molecule **2** and **b)** molecular packing of **2** (counter ions and solvent molecules have been omitted for clarity).

Table 1.2. Summary of crystallographic data for the molecule **2**

Parameters	**2**
Empirical formula	$C_{38}\ H_{50}\ N_4\ O_2(PF_6)_2$
Formula weight	884.76
T, K	300(2)
l, Å	0.71073

Crystal system	Orthorhombic
Space group	Aba2
a, Å	22.493(12)
b, Å	11.802(7)
c, Å	16.110(9)
a, deg	90
b, deg	90
g, deg	90
V, Å^3	4277(4)
Z	4
d_{calc}, Mg/m^3	1.374
F(000)	1840
Crystal size, mm	0.30 ´ 0.30 ´ 0.20
m (Mo_{Ka}), mm^{-1}	0.192
Theta range for data collection, °	6.22 to 53
Limiting indices	-28 ≤ h ≤ 17, -14 ≤ k ≤ 14, -29 ≤ l ≤ 18
Reflections collected/ unique	16670/ 4281
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	4281/1/263
Goodness-of-fit on F^2	1.111
Final R indices [I>2s(I)]	R1 = 0.0945, wR2 = 0.2370

R indices (all data)	R1 = 0.1464, wR2 = 0.2821
Largest diff. peak and hole, e-/Å^{-3}	0.383 and -0.186

Molecule **2** found to be crystallize in an orthorhombic fashion and it showed an intermolecular distance of 4.438 Å between the anthracene moieties in the different stacks and which results in the edge-to-edge excimer formation. While a distance of 9.986 Å was found for the anthracene moieties in the same stack. This large intermolecular distance obtained between the anthracene moieties of **2** validates with the lesser red shifted excimer emission maximum obtained for **2** in the solid state.

4. CONCLUSION

In conclusion, the photophysical properties of the synthesized molecules under different conditions indicate that these derivatives exhibit considerably different fluorescence properties in the solid state when compared to organic and aqueous media. Molecules **1** and **2** exhibits monomer emission both in organic and aqueous media, whereas dual emission were observed for **2** in the solid state. In the crystal packing, molecule **2** displayed more loosely stacked arrangement in the crystal. Presence of excimer like interactions in the solid state results in different photophysics in different media and hence these systems can have potential for the use as optoelectronic materials.

5. EXPERIMENTAL SECTION

5.1. GENERAL TECHNIQUES

The equipment and procedures for melting point determination and spectral recordings have been described elsewhere . All melting points were determined on a Mel-Temp II melting point apparatus. ^{1}H and ^{13}C NMR spectra were measured on a 300 MHz or 500 MHz Bruker advanced DPX spectrometer. HRMS were recorded on a JEOL mass spectrometer. The electronic absorption spectra were recorded on a Shimadzu UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. The fluorescence quantum yields were determined by using optically matched solutions. Quinine sulphate (F_f = 0.54) in 0.1 N H_2SO_4 was used as the standard . The quantum yields of fluorescence were calculated using the equation 2.1, where,

$$\Phi_u = \frac{A_s F_u n_u^2}{A_u F_s n_s^2} \Phi_s \qquad (Eq.\ 2.1)$$

A_s and A_u are the absorbance of standard and unknown, respectively. F_u and F_s are the areas of fluorescence peaks of the unknown and standard and n_s and n_u are the refractive indices of the standard and unknown solvents, respectively. F_s and Φ_u are the fluorescence quantum yields of the standard and unknown. Solid-state fluorescence measurements were carried out using the front face emission scan mode on a SPEX Fluorolog F112X spectrofluorimeter. The Xe-arc lamp was used to excite the samples placed in the sphere with 355 nm as the excitation wavelength. The quantum yield was determined by comparing the spectral intensities of the lamp and the sample emission as per literature reports.

5.2 MATERIALS

Anthracene, paraformaldehyde, HBr in acetic acid, sodium hydride and imidazole were obtained locally and used as received. Petroleum ether, ethyl acetate and methanol were used after the fractional distillation.

5.3. Synthesis of 9,10-bis((1*H*-imidazol-1-yl)methyl) anthracene (5)

To a reaction mixture of imidazole (0.5 g, 7.4 mmol) in dry THF (100 mL) was added NaH (0.33 g, 13.8 mmol) at 0 °C. After the reaction mixture was stirred for 30 min at 0 °C, 9,10-bis(bromomethyl)anthracene (**4**, 0.5 g, 1.4 mmol) was added. After additional stirring for 2 h at room temperature, the reaction mixture was poured into 100 mL of water and extracted with dichloromethane. The organic layer was then separated, dried over anhydrous sodium sulfate and concentrated to get a residue which was further purified by column chromatography over silica gel. Elution of the column with ethyl acetate yielded 0.37 g (78%) of **6**, which was then re-crystallized from a mixture of acetonitrile and ethyl acetate (4:1); mp 246-247 °C; ^{1}H NMR (300 MHz, DMSO-d_6) d 6.29 (s, 4H), 6.78 (s, 2H), 6.93 (s, 2H), 7.67 – 7.73 (m, 6H), 8.61 – 8.64 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) d 109.9, 113.6, 119.1, 124.7, 124.9, 128.3, 129.1, 130.1; HRMS (FAB): *m/z* calcd. for $C_{22}H_{19}N_4$: 339.4132, found 339.4508.

5.4. Synthesis of Molecule 1

To a solution of 9,10-bis((1*H*-imidazol-1-yl)methyl) anthracene (**5**, 0.25 g, 0.74 mmol) in a mixture of acetonitrile (100mL) and DMF (50 mL) was added bromoethane (0.081 g, 0.74 mmol). The reaction mixture was then refluxed for 24 h and after cooling to room temperature the precipitated product was filtered and washed with 30 mL dry acetonitrile. It was further purified by re-crystallization from acetonitrile to yield 180 mg

(40%) of **3**; mp 276-277 °C; ^{1}H NMR (500 MHz, Acetonitrile-d_3) d 1.37 (t, 6H), 4.04 (q, 4H), 6.39 (s, 4H), 7.32 (d, *J*=7Hz, 2H), 7.38 (s, 2H), 7.75 (q, 4H), 8.24 (s, 2H), 8.39 (q, 4H); ^{13}C NMR (125 MHz, Acetonitrile-d_3) d 14.0, 44.7, 45.3, 122.1, 123.9, 125.9, 127.7, 130.7, 134.6; HRMS (FAB) *m/z* calcd. for $C_{26}H_{28}N_4P_2F_{12}$: 541.4915, found 541.7100 [M – PF_6]$^{+}$.

5.5. Synthesis of molecule 2

To a solution of 9,10-bis((1*H*-imidazol-1-yl)methyl) anthracene (**5**, 0.25 g, 0.74 mmol) in a mixture of acetonitrile (100mL) and DMF (50 mL) was added 8-bromooctanol (0.154 g, 0.74 mmol). The reaction mixture was then refluxed for 24 h and after cooling to room temperature the precipitated product was filtered and washed with 30 mL dry acetonitrile. It was further purified by re-crystallization from acetonitrile to yield 340 mg (51%) of **4**; mp 260-261 °C; ^{1}H NMR (500 MHz, Acetonitrile-d_3) d 1.22 (m, 16H), 1.42 (m, 4H), 1.78 (m, 4H), 3.45 (t, 4H), 3.98 (t, 4H), 6.39 (s, 4H), 7.33 (s, 2H), 7.37 (s, 2H), 7.75 (q, 4H), 8.21 (s, 2H), 8.39 (q, 4H); ^{13}C NMR (125 MHz, Acetonitrile-d_3) d 25.1, 25.2, 28.1, 28.5, 29.0, 32.1, 45.4, 49.4, 61.2, 122.1, 122.3, 123.9, 125.9, 127.7, 130.7, 134.9; HRMS (FAB) *m/z* calcd. for $C_{38}H_{52}F_{12}N_4O_2P_2$: 886.77, found 741.3729 [M – PF_6]$^{+}$.

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