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Synthesis and Photophysical Properties of Pyrene-Based Green Fluorescent Dyes: Butterfly-Shaped Architectures

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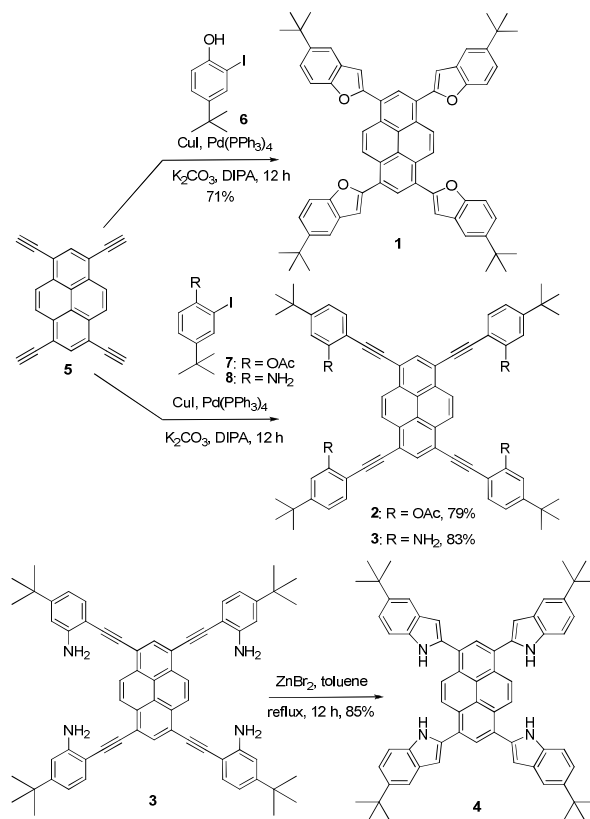
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A few pyrene-based fluorescent compounds were synthesized using Pd/Cu-catalyzed cross-coupling reaction. Photophysical properties of the π -conjugated pyrene derivatives were studied and the results indicate materials with high quantum efficiency and high extinction coefficient. No π stacking was observed in the crystal lattice. The molecules described here may be useful in developing sensors or imaging agents.

To date, significant efforts have been placed for the development of new fluorescent dyes for applications in biomedical imaging,¹ molecular sensors,² light emitting devices,³ nanoscience,⁴ biological chemistry⁵ and solar energy conversion.⁶ Such dyes showed efficient photoluminescence and ambipolar charge transport properties.⁷ Desired properties of fluorescent compounds include high absorption coefficients, high quantum yields, large Stokes shift, tunable absorption/emission profiles, high chemical and photochemical stability, solution processability without forming non-emissive aggregates, and low toxicity in biomedical applications. Few compounds, or families of compounds, satisfy all these requirements and thus design and synthesis of new dyes are considered. Inspired by interesting optical and electronic properties of functionalized conjugated fluorophores, Yamato and co-workers have synthesized a series of pyrene-based blue emitting fluorescent compounds.⁸ There are a few examples of fluorophores such as, 1,2,4,5-tetrasubstituted (phenylethynyl)benzenes,⁹ 1,2,4,5-tetravinylbenzenes,¹⁰ and 1,4-bis(arylethynyl)-2,5-distyrylbenzenes.^{11,12} Among the various polycyclic aromatic hydrocarbons (PAHs), pyrene and its derivatives have been widely utilized as fluorescent probes¹³ and fluorescent sensors¹⁴ due to many desirable photophysical properties such as long life time, low toxicity and easy access. The search for fluorescent molecules with high stability and high quantum efficiency led to the development of interesting molecules. Recently, some pyrene derivatives have been reported as electron donors and acceptors,^{15a} molecular sensors,^{15b} hole-transporting materials^{15c} and host blue-emitting materials.¹⁶

In this communication, we report the synthesis and photophysical properties of pyrene-based butterfly-shaped, π -conjugated green-light-emitting compounds. The target molecules were prepared using Sonogashira coupling in high yield. These

compounds showed absorption maxima around 450 nm and emission maxima around 510 nm. In addition, the target molecules are soluble in common organic solvents such as acetonitrile, tetrahydrofuran, dichloromethane and chloroform, which implies low intermolecular interaction. No aggregation was observed in common solvents at different concentrations.



Scheme 1. Synthesis of fluorophore 1, 2, 3 and 4.

Moreover, the single crystal X-ray diffraction showed no π stacking in the solid state due to incorporation of four ^tBu groups on the periphery of the pyrene core.

As delineated in Scheme 1, the fluorophores were synthesized by Pd/Cu-catalyzed cross coupling reaction between 1,3,6,8-tetraethynylpyrene **5**¹⁷ and corresponding iodo-aryl derivatives.^{18,19} For the synthesis of fluorophore **1**, 4-*tert*-butyl,2-iodophenol **6**¹⁸ was identified as the appropriate partner. Therefore, treatment of tetraethynylpyrene **5** with **6** using Pd(PPh₃)₄, CuI and K₂CO₃ condition accomplished the desired compound **1** in excellent yield, where Pd plays a dual role; initially catalyzing Sonogashira coupling and followed by concomitant cyclization *via* activation of alkyne and reaction with adjacent hydroxyl group. Similar conditions were used for other compounds to afford **2** and **3** in 79 % and 83% yield respectively.

In case of compound **4**, the same conditions did not yield the desired product. The intramolecular cyclization of product **3** was achieved by carrying out the reaction under Lewis acid metal-mediated cyclization. After extensive studies, InCl₃,²⁰ Ag(OTf)₂²¹ and ZnBr₂²² were found to be successful to give the target compound **4** in 85% yield. The structures of new pyrene derivatives were fully characterized using ¹H NMR, ¹³C NMR, FT-IR spectroscopy and mass spectrometry. The thermal properties of all compounds were examined by thermo gravimetric analysis (TGA) under a nitrogen atmosphere and all compounds showed have high thermal stability. The compound **4** was stable up to 600 °C (Figure 1).

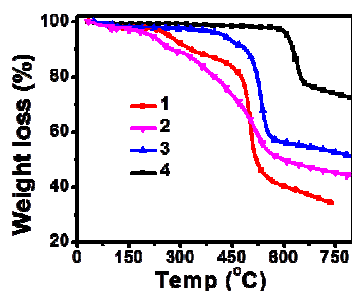


Figure 1. Thermogravimetry analysis for compound **1**, **2**, **3** and **4**

The absorption and emission spectra of compound **1** and **4** were recorded in CH₂Cl₂ solutions (Figure 2). The absorbance was measured at ambient conditions for all compounds. Absorption maxima were observed at 350 and 450 nm for compounds **1** and **4**, respectively (Fig. S1, S2 in the ESI). In case of compound **2** and **3**, more than one absorbance maxima were observed (Fig. S3, S4 in the ESI). In all cases, the excitation wavelength corresponded to the 2nd absorbance maxima and following Stokes shift were observed: 60 nm

Table 1. Photophysical properties of compounds **1**, **2**, **3** and **4**^a

compd	λ_{\max} abs (nm)	λ_{\max} PL (nm)	Φ_f^b solns	ϵ (M ⁻¹ cm ⁻¹)	T _d ^c (°C)
1	450	510	0.70	67200	320
2	440	485	0.77	46800	264
3	460	525	0.60	61800	480
4	440	510	0.69	38800	625

^aPhotophysical measurements in CH₂Cl₂ solution at room temperature; ^bDetermined by comparison with fluorescein ($\Phi = 0.79$) in ethanol; ^cDecomposition temperature (T_d) obtained from TGA measurements with a heating rate 10 °C min⁻¹ under N₂; ϵ , extinction coefficient; Φ_f , fluorescence quantum yields.

for **1**, 45 nm for **2**, 65 nm for **3** and 70 nm for **4**. Furthermore, concentration dependent studies were carried out in CH₂Cl₂ for compound **1** (Fig. S5 in the ESI) as well as for compounds **3** and **4**

(Fig. S6, S7 in the ESI) to check π - π stacking interactions induced aggregation in solution. The concentration dependent studies confirmed the absence of excimers and can be justified by enhancement of emission intensity upon increasing the concentration of fluorophores. The key photophysical properties of pyrene derivatives are summarized in Table 1, which reveals that these compounds can be very promising molecular probes with high quantum yields, molar extinction coefficient as compared to similar structures in literature.^{8a,23}

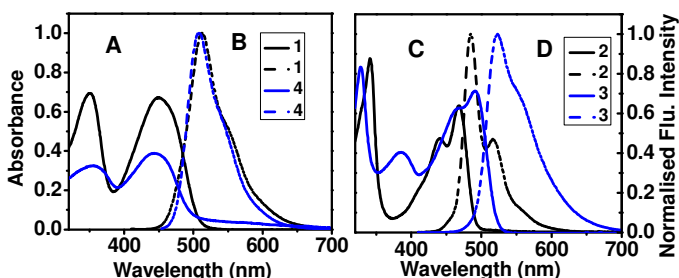


Figure 2. The UV-vis absorption spectrum in 10 μ M and normalized fluorescence spectrum in 1 μ M of **1**, **4** (A, B) and **2**, **3** (C, D) recorded in CH₂Cl₂.

The solvent dependent photophysical properties of all chromophores were carried out in order to understand the excited state dipole moment. No change in absorbance maximum was observed with change in polarity of solvent, non-polar solvent cyclohexane to nonprotic polar solvent, dimethyl formamide. The fluorescence of compound **3** was partially quenched due to electron transfer (ET) of free amine to the excited pyrene core.²⁴ Spectrophotometric titration experiments were carried out with H⁺ ions to gain more insight into photo-induced electron transfer (PET) process in compound **3** (Figure 3). It is clear that the intensity of the absorption bands at 335 nm and 460 nm increased while intensity of peak at 380 nm decreased with two isosbestic points at 350 and 405 nm with increase in amounts of H⁺ ions. The intensity of emission enhanced upon increasing the concentration of H⁺ due to protonation of free amino groups in the molecule.

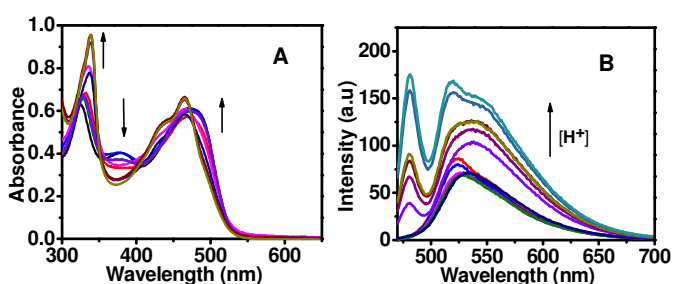


Figure 3. The absorption (A) and emission spectra (B) of compound **3** (10 μ M) in EtOH with a pH values of 6, 5, 4, 3, 2, 1.8, 1.6, 1.4, 1.2, 1, 0.8, 0.6, and 0.2.

Attempts to grow high quality single crystals from all molecules only provided good quality crystals of target molecule **1**. The crystal is monoclinic with a space group P2(1)/c. The asymmetric unit contains half a molecule of the compound C₆₄H₅₈O₄. The molecular packing of **1** is shown in Figure 4. The distance between the two adjacent pyrene units inside the lattice is about 5.72 Å. From the packing pattern, it is clear that there were no π - π interactions in the

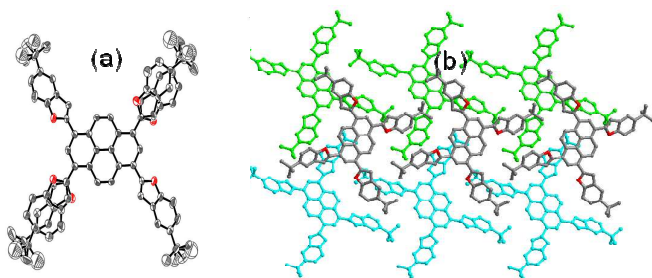


Figure 4. (a) ORTEP representation of molecule **1** with 40 % probability (left) and (b) molecular packing viewed down close to a axis (right). The crystal was grown by a slow evaporation of CHCl₃/hexane solution.

solid state (Figure 4b). Hence, this property endows them with the bright luminescence in the solid state. The structure was refined with a two part disordered structure, resulting in ratio of 60:40 of the two parts. Final R values are $R_1 = 0.0775$ and $wR_2 = 0.1968$ for 2 theta up to 50° (Table 1, in the ESI).

To gain further insight into the geometric, electronic and optical properties of pyrenes dyes, hybrid density functional theory (DFT) with B3LYP level, 6-31G(d)²⁵ as a basis set was used for geometry and energy optimization. The geometry and energy optimized structures of the compounds **1** and **4** (Fig. S9, in the ESI) and the distribution of Frontier orbitals were calculated (Figure 5). The HOMO of compounds **1** and **4** is distributed on pyrene and fused substituents. In both cases, the LUMO is mainly on the pyrene core and partially scattered on the substituents; the nodal plane passing through pyrene 2 and 7 positions perpendicular to molecular plane. The HOMO of furan fused compound **1** is found to be at -4.92 eV where pyrrole fused compound **4** is calculated to be -4.89 eV. In the case of LUMO, both compounds **1** and **4** have similar values at -2.18 eV and -2.15 eV respectively, leading to same energy gap (2.74 eV). These calculated results agree with photophysical data.

In conclusion, we have successfully synthesized and characterized a relatively novel class of pyrene-based, fluorescent compounds. The absorption and emission spectra of these compounds indicate that the extension of π conjugation through phenylacetylenic, indole and benzofuran substituents serves to shift the wavelength of absorption and fluorescence emission towards green segment of the visible spectrum. From a single crystal X-ray diffraction analysis indicates that the four bulky *t*-Bu groups on periphery of chromophores play an important role to inhibit the π - π stacking between the neighbouring pyrene units. These molecules exhibit high stability, good solubility in most of the common organic solvents and emit very bright, green fluorescence.

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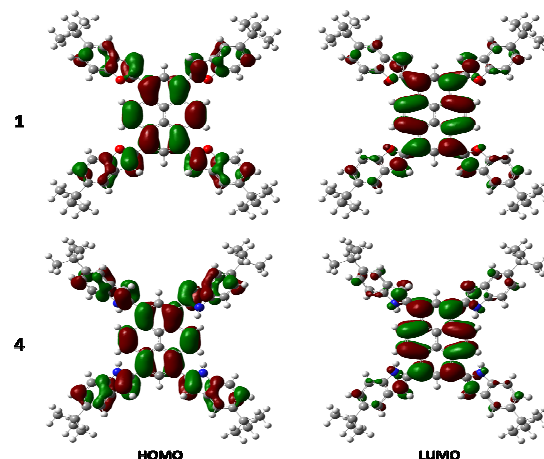


Figure 5. Frontier molecular orbitals of **1** and **4** molecules calculated by DFT at B3LYP/6-31G(d) level.

Notes and references

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Electronic Supplementary Information (ESI) available: NMR spectra of all new compounds as well as additional photophysical characterisation.

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