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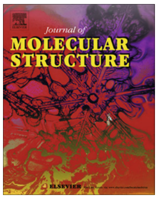

H-aggregation of the amphiphilic dye TDPI: Photophysical, electrochemical, DFT and SAXS studies

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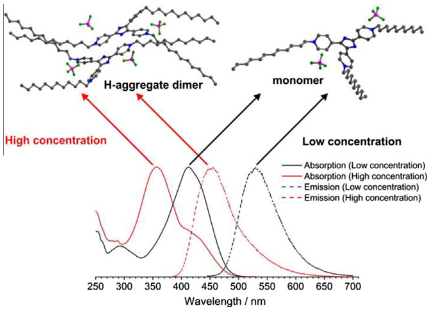
HIGHLIGHTS

- Synthesis and characterization of the new amphiphilic dye TDPI.
- Photophysical characterization of H-aggregation with solvent effects.
- SAXS studies of the dye aggregation revealing fractal structures.
- DFT calculations of large structures including self-assembly interactions.

GRAPHICAL ABSTRACT



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Dedicated to the memory of Juliano Vicente a great friend and a gifted scientist who suddenly died at 36 years of age on December 30, 2013. We will miss Juliano very much.

Keywords:
H-aggregation
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ABSTRACT

A new amphiphilic dye 2,4,5-tris(1-dodecylpyridinium-4-yl)imidazol-1-ide tetrafluoroborate (TDPI) was synthesized and characterized by ^{1}H and ^{13}C NMR, ESI-TOF mass spectra and elemental analysis. The photophysical behavior of TDPI was investigated by means of UV–Vis and fluorescence spectroscopy techniques. The results show a solvent-dependent blue-shift absorption and emission which were assigned to an H-aggregation. The calculated dimerization aggregation constant is 10 times bigger in dichloromethane than in acetonitrile, which is probably due to stronger ionic pair stabilization in low dielectric media. The structural characteristics of the formed aggregate were also investigated by SAXS analysis, revealing a surface fractal structure for all solvents. DFT calculations were used to investigate the photophysical properties of the monomer and the aggregate dimer. The TD-DFT calculations successfully described the electronic spectra of the monomer, but failed to simulate the dimer spectra as expected for this type of system. However, the TD-DFT of the dimer corroborates the experimental observed blue-shift tendency.

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1. Introduction

Dye aggregation has been observed in many different systems such as pyrene [1,2], perylines bisimides [3], porphyrin [4], cyanine dyes [5–8], and tetrazoles [9], among others [10]. Normally,

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molecules with extended π-systems undergo aggregation in solution under increasing concentration. The most common spectral changes observed in aggregation are the deformation of the absorption and emission bands. Modification of spectroscopic properties upon aggregation can be assigned to intermolecular excitonic interactions within the aggregates due to coupling of the optical transitions of individual monomers [9,11]. The red shift is attributed to J-aggregation (J denotes Jelley in reference to E.E. Jelley who was a pioneer in the field [12,13]), while the blue shift is associate to an H-aggregation (H denotes hypsochromic). The J- and H-aggregates form structures where the molecular planes are stacked side by side and face to face, respectively. The angle (α) between the transition moments of the monomer molecules and line joining the centers of the molecular planes defines the aggregate type, for J-aggregate $0 < \alpha \leqslant 54.7°$ and H-type $54.7 < \alpha < 90°$. Blue-shift of the absorption spectra with increasing concentration is also sometimes referred to as static excimer dimer formation, due to the aggregation of the monomer molecules in the ground state [14,15]. Aggregates and fractal structures derived from many different materials have been extensively characterized by small angle X-ray scattering (SAXS) [16–19], which makes this technique suitable for the investigation of the self-assembly interactions.

The molecule 2,4,5-tris(4-pyridinyl)-imidazole (Htpim) [20,21] is a rigid tripodal ligand with three pyridine coordination sites, which has been used in the synthesis of luminescent metal–organic coordination polymers with transition d^{10} metals: Cu (I), Cd (II), Zn (II) and Ag (I) [22–24]. Yang investigated the spin-crossover effect on the iron (II) complex $[Fe(3PY\text{-}im)_2(NCS)_2]\cdot 7H_2O$ (3PY-im = Htpim) and found that this compound undergoes incomplete transition spin behavior [25].

In this work the Htpim molecule was modified by alkylation of the pyridine groups generating the amphiphilic compound 2,4,5-tris(1-dodecylpyridinium-4-yl)-imidazol-1-ide (TDPI). The TDPI structure has four main components: three 1-dodecylpyridinium cations and an imidazolate anion, resulting in a dicationic compound. A detailed study about the aggregation of TDPI and its photophysical consequences in solution was carried out by absorption spectroscopy, steady-state fluorescence spectroscopy, electrochemistry, SAXS and DFT calculations.

2. Experimental section

2.1. Materials

All reagents and solvents for synthesis and analysis were of analytical and/or spectroscopic grade and used without further purification. The 2,4,5-tris(4-pyridinyl)imidazole (Htpim) was prepared as described elsewhere [20,21].

2.2. Synthesis of 2,4,5-tris(1-dodecylpyridinium-4-yl)imidazol-1-ide tetrafluoroborate (TDPI(BF_4)$_2$)

A mixture of 500 mg (1.67 mmol) of Htpim and 1.60 mL (6.18 mmol) of dodecyl bromide in 25 mL DMF was heated up to 120 °C under stirring for 72 h. The solvent was removed at low pressure and the solid was dispersed in a hexane solution, resulting in an orange solid which was recrystallized in 10% tetrafluoroborate aqueous ethanol solution. The resulting solid was recrystallized as monohydrate in dichloromethane (1.28 g, 78%) as small yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (mt, 9H, $C\underline{H}_3$), 1.25 (mt, 42H, $C\underline{H}_2$), 1.36 (mt, 12H, $C\underline{H}_2$), 2.01 (mt, 6H, $C\underline{H}_2$), 4.47 (mt, 4H, CH_2), 4.54 (mt, 2H, $C\underline{H}_2$), 8.00 (d, ^3J = 6.3 Hz, 4H, H_c), 8.32 (d, ^3J = 6.3 Hz, 2H, H_b), 8.60 (d, ^3J = 6.3 Hz, 4H, H_d), 8.72 (d, ^3J = 6.3 Hz, 2H, H_a). ^{13}C NMR (100 MHz, $CDCl_3$): 14.3, 18.7, 22.9, 26.6, 29.5, 32.1, 86.8, 122.3, 124.8, 141.0, 148.1, 149.7, 152.0. ESI-TOF-MS m/z = 892.76 ($[TDPI^{2+} - BF_4^-]^+ = [C_{54}H_{87}BF_4N_5]^+$) calcd. 892.70; 402.84 ($[TDPI^{2+} = [C_{54}H_{87}N_5]^{2+}$) calcd. 402.83. Anal. Calc. for $C_{54}H_{87}B_2F_8N_5 \cdot 2H_2O$: C, 63.84; H, 9.03; N, 6.89. Found: C, 63.00; H, 9.00; N, 6.90.

2.3. Methods

^{1}H and ^{13}C NMR spectra were collected on a Varian AS400 spectrometer. Elemental Analyses were carried out on a CHN Varian EA 1100. The UV-spectra (1 cm quartz cell) were recorded on Varian Cary 50 with temperature controlled by thermostatic bath at 25.0 ± 0.1 °C. Mass spectra were obtained in positive mode on a micromass LCT time of flight MS. Concentration dependence of the emission spectra was recorded in a Varian Cary Eclipse spectrometer. The quantum yield was determined as described in the literature, using a quinine sulfate solution in H_2SO_4 0.5 mol L^{-1} (Φ = 0.546) as standard, through Eq. (1) [26].

$$\Phi_f^i = \frac{F^i f_s n_i^2}{F^s f_i n_s^2}\Phi_f^s \qquad (1)$$

where Φ_f^i and Φ_f^s are the photoluminescence quantum yield of the sample and reference, respectively. F^i and F^s are the integrated (area) emission spectra of sample and standard; f_x is the absorption factor ($f_x = 1 - 10^{-A_x}$, where A_x = absorbance) and n_i and n_s are the refractive indices for sample and reference, respectively. The electrochemical experiments were carried out with deaerated solutions of TDPI(BF_4)$_2$, in dry MeCN, MeOH, and CH_2Cl_2 using 0.1 mol L^{-1} tetrabutylammonium phosphate as electrolyte support for MeCN and MeOH and tetrabutylammonium perchlorate for CH_2Cl_2. The experiments were performed in a BASi EC epsilon, using glassy carbon as a work electrode, Ag/AgCl as a reference electrode and a Pt wire as a counter electrode. The potentials were corrected using ferrocene as an internal standard (Fc/Fc$^+$: 0.400 V versus NHE) [27]. SAXS experiments were performed on the D11A-SAXS beamline of the Brazilian Synchrotron Light Laboratory (LNLS-Campinas, SP, Brazil), with λ = 1.488 Å and $0.05 < q < 3.33\ nm^{-1}$, where $q = 4\pi\ \sin(2\theta)/\lambda$; q is the scattering vector, θ is the scattering angle, and λ is the X-ray wavelength. The liquid samples were dissolved in MeCN and MeOH at a concentration of 10^{-2} mol L^{-1} and injected at room temperature into a specifically designed liquids cell composed of two mica windows separated by a distance of 1 mm, positioned orthogonally to the beam. Powder samples were mounted between two sheets of Kapton foil. The 2D scattering patterns were collected after an exposure time of 500 s. In all cases, the 2D images were corrected by the FIT2D software developed by Hammersley [28], taking into account the detector dark noise and normalized by the sample transmission considering the 360° azimuthal scan. The resulting $I(q)$ versus q curves were corrected by the subtraction of the scattering of the pure solvent and placed on an absolute scale using as standard. The fitting procedures were carried out using the SASfit software which makes use of the least-squares fitting approach to minimize the chi squared (χ^2) parameter. The SASfit software package was developed by Kohlbrecher, and it is available free of charge [29].

2.4. Computational details

Ground-state structure optimizations were carried out by using the non-hybrid DFT method PBE [30] and the split valence def2-SVP basis set [31]. The resolution identity – RI [32] implemented in TURBOMOLE 6.1 [33] was used to reduce the CPU time. Solvent effects were included in all calculation by using the COSMO method [34], MeCN (ε = 35.688) and all default parameters for the cavity from TURBOMOLE. Fine quadrature grids (size m4) were employed. Energies converged to 10^{-6} hartree and gradients were converged

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