ORGANIC LETTERS

2009
Vol. 11, No. 22
5106−5109

Dramatic Red-Shifted Fluorescence of [2.2]Paracyclophanes with Peripheral Substituents Attached to the Saturated Bridges

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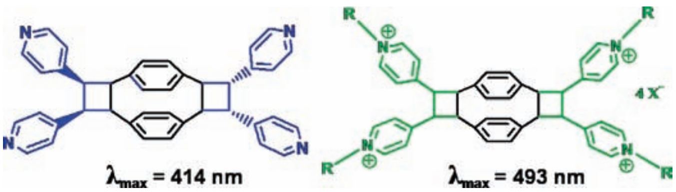
Received August 17, 2009

ABSTRACT



A bridge-substituted [2.2]paracyclophane obtained from the organic solid state exhibits a dramatic red shift in fluorescence relative to [2.2]paracyclophane. A further red shift occurs upon alkylation of the pyridylcyclobutyl bridges. Our results demonstrate that [2.2]cyclophanes substituted at the bridge, despite not being attached via the extended π-system, are promising building blocks in the development of optical materials.

Although [2.2]paracyclophane (**pCp**) has been known for almost 60 years, the physical properties of the molecule remain a rich area of inquiry and study.[1] Initial interests in **pCp** spawned from the reactivity of the strained molecular structure; however, much focus has recently shifted to controlling photophysical properties[2] for the development of device-based applications. Applications of the stacked architecture of **pCp** as a bichromophoric system to study through-space delocalization have been recently developed.[3] In such applications, the strained and stacked structure of the cyclophane is utilized not only to hold two chromophores in close proximity but also to take advantage of intrinsic transannular charge transfer. By invariably attaching chromophores orthogonally to the decks of **pCp**, conjugated frameworks have been produced that enhance internal charge transfer (ICT) leading to varied photophysical properties. ICT is an electronic transition wherein charge is shuttled between electronically donating and accepting regions of a molecule.[4] Compounds demonstrating ICT possess distinct donor and acceptor groups typically connected by a π-electron conjugated path. **pCp**-based chromophores have been modules for ICT studies that occur across the transannular gap.[4] Related applications of **pCp** have been developed in areas of asymmetric synthesis,[5] biomedicine,[6] nanotechnology,[7] and catalysis.[8] Whereas the vast majority of applications of **pCp** have emerged based on orthogonal derivatization of the

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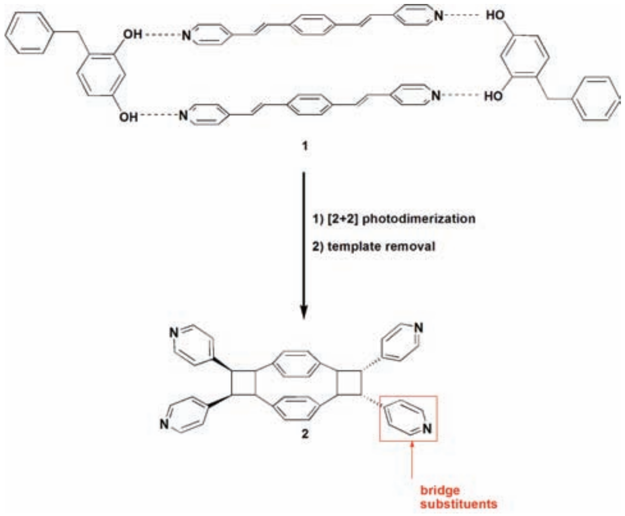
10.1021/ol901907j CCC: $40.75

π-stacked decks, less focus has been placed on substituents installed on the saturated bridges, which is presumably due to the lack of useful synthetic methodologies that extend the aliphatic system. Indeed, the controllable synthesis of [2.2]cyclophanes with tunable optical properties and optimized ICT can lead to novel materials with applications for semiconductors,[9] biosensors,[10] organic dyes,[11] and cellular diagnostics.[12]

Recently,[13] we have shown how co-crystallization of a substituted resorcinol with *p*-bis[2-(4-pyridyl)ethenyl]benzene (**1**) and subsequent double [2 + 2] photoreaction in the organic solid state affords tetrakis(4-pyridylcyclobutyl)-**pCp** (**2**) stereospecifically, in quantitative yield, and in gram amounts (Scheme 1). The photoreaction makes available a **pCp** that is difficult to achieve using more conventional approaches to organic synthesis, resulting in a bridge-substituted **pCp** with pyridylcyclobutyl groups that border and extend the stacked benzene rings via saturated linkages.

Scheme 1. Solid-State Synthesis of Peripherally Substituted **pCp 2**



During our pursuits to study optical properties of our reactive solids,[14] we developed an interest to study the photophysical properties of **2**.[3] We envisioned that the distal 4-pyridyl groups could act as a chromophore to probe optical properties of the stacked cyclophane core. In studies to determine the impact of interchromophore delocalization on fluoresence,[15] stilbene donor and/or acceptor units were attached to **pCp**, with wide ranges of absorbance (λ = 400−450 nm) and fluorescence (λ = 460−560 nm) being observed. Owing to the high degree of sensitivity of fluorescence to molecular structure, we sought to investigate whether the 4-pyridyl groups of **2**, and derivatization of the chromophores, could affect the fluorescence of the cyclophane *in the wake of* being attached via the saturated cyclobutyl bridges.

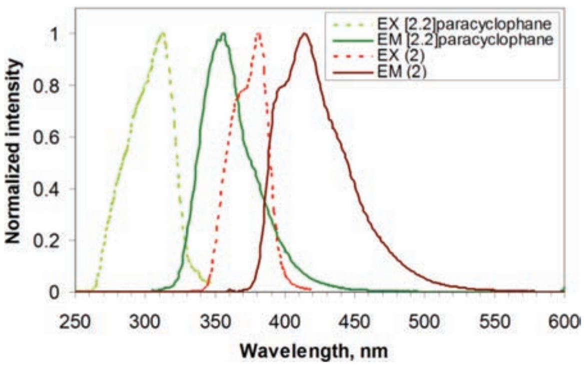


Figure 1. Excitation (EX) and emission (EM) spectra of [2.2]paracyclophane and **2** in DMF at micromolar concentrations.

Herein, we report the synthesis of peripherally substituted **pCps** obtained from the solid state. We show that paracyclophane **2** exhibits red shifts on the order of 60 nm in both absorption and emission compared to **pCp**. Additionally, we show that facile alkylation of the lateral 4-pyridyl groups results in additional strong red shifts in fluorescence up to 80 nm.

The starting point of our investigation is **2**, which is prepared from a template-directed solid-state reaction of diene **1**.[16] Comparisons of the emission spectrum of **2** with commercially available **pCp** and the parent diene **1** revealed that **2** exhibits a large red shift in fluorescence ($\lambda_{\max(\mathrm{em})}$ of 414 nm as opposed to 356 nm) relative to **pCp**, yet at a position comparable to **1** ($\lambda_{\max(\mathrm{em})}$ = 401 nm).[17] These observations were surprising given that the pyridine rings are attached to the cyclophane core through saturated, as opposed to delocalized, linkages while the cyclobutyl rings effectively disrupt the extended conjugation of the parent diene **1**. The red shift in fluororesence also corresponds to a longer excitation maximum relative to **pCp** (380 nm versus 313 nm) (Figure 1). Collectively, these observations suggest that the cyclobutanes of **2** act as efficient through-bond donors that permit withdrawl of electrons from the strained and stacked aromatic core to the distal electron-poor py-

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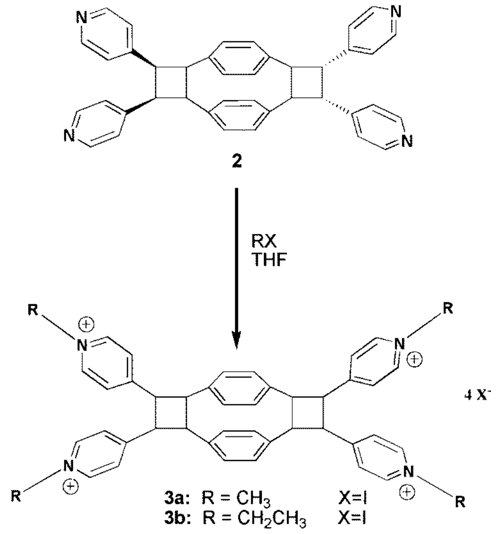
Scheme 2. Synthesis of *N*-Alkylated **pCp**s **3a** and **3b**



ridines.[18] Given the fact that large quantities of **2** are available and that pyridine rings can be easily derivatized, we sought to determine whether modifying the pyridines can affect electron donation from the dicyclobutyl-**pCp** core and, thus, provide improved conditions for ICT that impact the fluorescence.

To determine optical effects of peripheral derivatization, *N*-alkylated paracyclophanes **3a** and **3b** were prepared. In a typical experiment, reaction of **2** with the corresponding alkyl iodide in tetrahydrofuran afforded the tetraiodo salt in quantitative yields (Scheme 2). ^{1}H NMR spectroscopy confirmed that tetraalkylation occurred for **3a** and **3b**. In the resulting spectra, the α-pyridyl and *β*-pyridyl protons shifted to 8.82 and 8.09 ppm, respectively. Additional shifts were seen for the cyclobutyl protons, which appear as sharp doublets at 5.25 and 4.84 ppm.[19]

Fluorescence spectroscopy of the alkylated paracyclophanes **3a** and **3b** revealed a large bathochromic shift upon alkylation. With an excitation wavelength of 380 nm,[20] broad emission peaks for both **3a** and **3b** appeared at 493 nm (Figure 2). These observations are comparable to **pCps** with stilbenoid chromophores *conjugated* to the stacked cyclophane decks that exhibit maximum emissions of approximately 430 nm,[21] yet less than those involving strong acylic donor and acceptor groups (e.g., NO_2 and NR_2) attached at the termini of the stilbenoid arms.[22]

The emission properties of **2** can be attributed to electron donation by the dicyclobutyl-**pCp** core outward to the electron-accepting peripheral pyridines. Indeed, the fused nature of the dicyclobutyl-**pCp** network is considerably strained and as a result can be considered an electron-donor scaffold.[4] The larger red shifts in the cases of derivatives **3a** and **3b** can be attributed to the quaternization of the pyridyl N-atoms. The derivatization allows for strong polarization over the entire cyclophane molecule by increasing the electron-accepting properties of the distal 4-pyridyl groups. The alkylation of **2** thus enhances ICT wherein electrostatic interactions account for the relatively large red shifts in absorption and emission.[23] For **3a** and **3b**, the pyridinium substituents likely withdraw electron density from the **pCp** fluorophore through the strained cyclobutane bridges, resulting in a nonconventional ICT. These observations involving the pyridinium ring system are consistent with optical properties of 1,8-naphthalimide-based organic dyes,[24] wherein alkylation also resulted in bathochromic shifts of fluorescence involving a fully conjugated system.

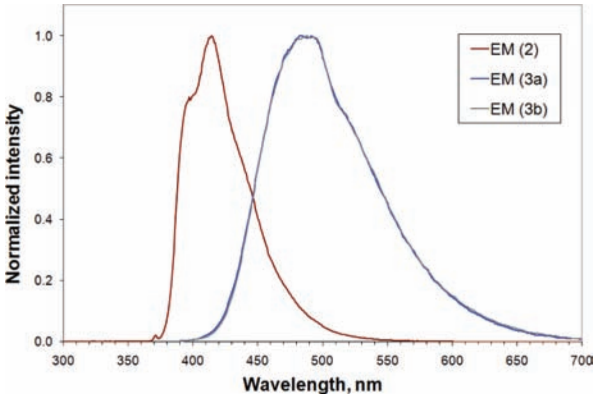


Figure 2. Emission spectra of **2** and *N*-methyl (**3a**) and *N*-ethyl (**3b**) derivatives in DMF at micromolar concentrations.

To gain further insight into the photophysical properties of the substituted cyclophanes, density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were conducted. In the optimized structure of **2**, the electron clouds of the HOMO and LUMO are localized on the **pCp** core, while the LUMO+1 is localized almost exclusively over the pendant pyridine rings.[25] For cationic **3a** (Figure 3), the electron clouds of the LUMO are, in contrast to **2**, localized on the pyridines, with the HOMO being localized, similar to **2**, on the **pCp** core. Collectively, these observations are consistent with the **pCp** core acting as an electron donor whereby electronic excitation leads to an increase in electron density toward the electron-poor pyridine groups, with the relative positions of the LUMOs reflecting the gradual red shifts in fluorescence. Electron density, albeit to a lesser

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[18] We note that related dicyclopropyl-**pCp** shows lower energy ionization potentials relative to **pCp** as a result of the interaction of cyclopropane σ orbitals with the paracyclophane π system (see Gleiter, R.; Schaefer, W. *Acc. Chem. Res.* **1990**, *23* (11), 369375) .

[19] Studies are underway to determine the stereochemistry around the cyclobutane rings of **3a** and **3b**.

[20] The maximum excitation wavelengths for **3a** and **3b** are 422 and 427 nm, respectively.

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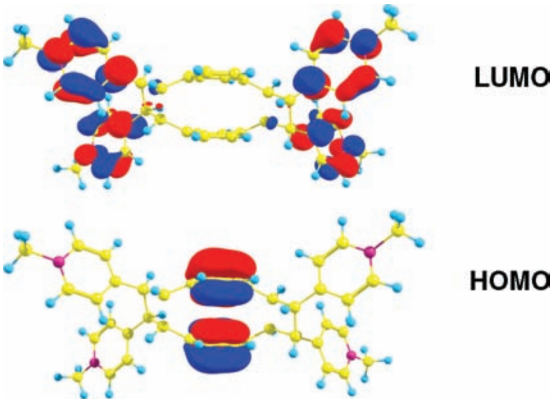

Figure 3. HOMO and LUMO of **3a** obtained using DFT calcuations at the B3LYP/6-31G(d) level.

extent, is also observed on the two cyclobutane rings at both HOMO and LUMO levels, which lends a measure of support for the cyclobutanes acting as through-bond donors.

In this report, we have demonstrated strong red-shifted fluorescence of a **pCp** via installment of substituents at the saturated bridges. Laterally substituted **2** exhibits shifted fluorescence despite the chromophores being attached by saturated cyclobutyl rings. Alkyl functionalized **3a** and **3b** displayed further bathochromic behavior in both excitation and emission, which can be attributed to polarization of the pyridinium ring. These results augur well for employing laterally substituted **pCp** in the development of optical device-based applications (e.g., molecular sensing, nonlinear optics).

Acknowledgment. We are grateful to the National Science Foundation (L.R.M., DMR-0801329) for funding.

Supporting Information Available: Experimental procedures and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL901907J