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Tetrahedral rigid core antenna chromophores bearing bay-substituted perylenediimides

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ABSTRACT

Two new representative methane- and adamantane-centered ‘antenna’ tetramers bearing bay-substituted π-conjugated phenylethynyl-perylenediimides (PDICCPh) as chromophoric subunits, *tetrakis*-[1-(4-ethynylphenyl)-*N*,*N*′-bis(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic diimide]-methane (**1**) and *tetrakis*-1,3,5,7-[1-(4-ethynylphenyl)-*N*,*N*′-bis(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic diimide]-adamantane (**2**), have been synthesized and their structural aspects have been thoroughly investigated by NMR spectroscopy. These PDI tetramers (**1** and **2**) represent the first successful example of incorporating the bay-substituted phenylethynyl-perylenediimides into the large rigid core tetrahedral frameworks. In these PDI tetramers, dynamic NMR experiments revealed the existence of perylene-centered conformational dynamic equilibrium ($\Delta G^{\neq}=15-17$ kcal/mol), the primary cause of the observed spectral broadening in conventional ^{1}H NMR spectra (295 K). In addition, PDI tetramers **1** and **2** were found to possess exceptional (photo)chemical stability, and their corresponding photophysical properties ($\varepsilon_{max}\sim 180{,}000$; $\tau_{FL}=6.9$ ns; $\Phi_{FL}\sim 60\%$) make them viable candidates for various photonic applications and are in good agreement with other related multichromophoric PDI-based systems.

1. Introduction

Over the years, perylenediimide-based (PDI) chromophoric systems have been the subject of immense research efforts thanks to their unique combination of chemical, photochemical, and photophysical properties.[1–6] Multichromophoric systems incorporating a broad spectrum of PDI molecules proved to be excellent models for exploring fundamental and applied aspects of diverse photonic, electronic, and photovoltaic materials.[7–16] In addition, various carefully designed PDI-based molecular compositions have been utilized as probes of photoinduced ultrafast processes (e.g., those occurring in natural photosynthetic systems), thus leading to a better understanding of underlying quantum coherence, excitation energy flow and excitonic coupling effects.[17–25] Similarly, molecular PDI acceptor chromophores have been exploited in numerous upconversion photochemistry compositions.[10,12,26]

The synthetic accessibility of PDI functionalization chemistry (either at the imide position or in the bay region) allows one to construct multichromophoric assemblies with a desired set of functional properties.[8,27–29] The goal of the present work is to utilize the highly emissive PDI chromophores with extended π-conjugation in the bay region as building blocks to construct three-dimensional, electronically coupled molecular systems (tetrameric ‘antennas’) that would exhibit relatively strong intramolecular electronic interactions and desirable photophysics as a result of being held together by a tetrahedral rigid core. In this particular case, the extent of intramolecular electronic coupling can be manipulated by varying the size of the rigid core: methane vs. adamantane. In addition, as prototype photochemically robust antenna chromophores and potentially viable alternatives to fullerenes, these PDI tetramers may be of particular interest for photovoltaic applications as well as in photochemical upconversion.[7,30–32] Noteworthy, the rigid cores of this nature have been extensively explored in a variety of visible light sensitizers (both pure organic and transition metal-based) designed for the covalent surface functionalization of wide bandgap semiconductor nanomaterials (e.g., TiO_2, ZnO).[33–37]

PDI-based molecular systems are also well known to display solvent-dependent aggregation behavior, thus making them perfect candidates for probing various energy and electron transfer pathways in both aggregated and non-aggregated forms.[38–42] However, we note that any detailed discussion of the associated excited state photochemistry of synthesized PDI tetramers is well beyond the scope of the present work and will be the subject of a separate in-depth contribution. To date, there is only a handful of (photophysical) studies on PDI-containing tetrahedral assemblies

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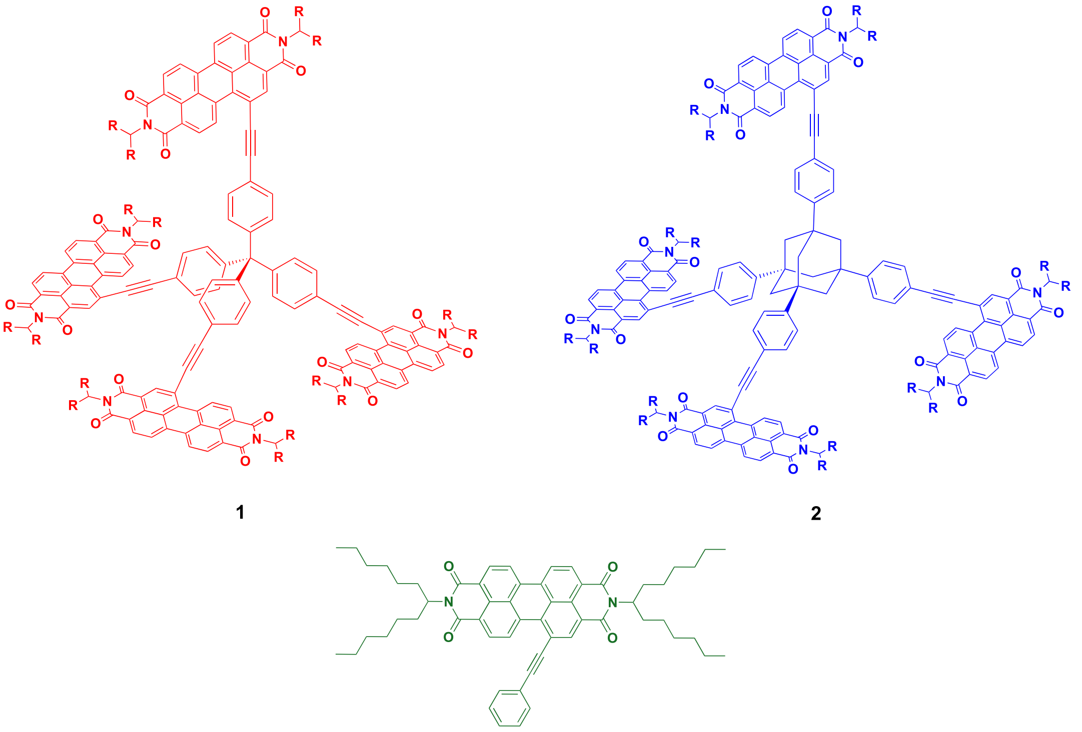
and, in most cases, these PDI architectures have been synthesized utilizing a relatively straightforward imide condensation chemistry between the amine-functionalized rigid core(s) and the corresponding perylene dianhydride(s).[1,41,43] Moreover, the successful examples of tetrameric structures incorporating the bay-substituted PDIs have been quite scarce in the literature and the few available reports are mainly based on studying the properties of phenyl-PDI-containing structures.[44,45] In our case, it is expected that the incorporation of phenylethynyl-perylenediimides (PDICCPh) bearing extended π-conjugation into tetrahedral rigid core structures would result in the substantial enhancement of their corresponding light-harvesting properties in a broader spectral window and thus may be advantageous in various photonic applications as compared to other related PDI-based oligomeric structures.

In this manuscript, we report the synthesis, NMR structural characterization and photophysical properties of two representative methane- and adamantane-centered tetramers bearing bay-substituted π-conjugated phenylethynyl-perylenediimides (PDICCPh) as chromophoric subunits that also incorporate solubilizing 1-hexylheptyl functionalities at the imide positions, *tetrakis*-[1-(4-ethynylphenyl)-*N*,*N*′-bis(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic diimide]-methane (**1**) and *tetrakis*-1,3,5,7-[1-(4-ethynylphenyl)-*N*,*N*′-bis(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic diimide]-adamantane (**2**). To delineate the electronic and structural effects associated with the tetrahedral assembly of four PDICCPh subunits into a large tetrameric framework, **1** and **2** are compared to the model monomer **3**, a single structural subunit of each target PDI tetramer. The corresponding chemical structures of the newly synthesized PDI tetramers **1** and **2**, as well as the model PDI monomer **3** are presented in Fig. 1. To the best of our knowledge, this work represents the first example when the bay-substituted phenylethynyl-perylenediimides (PDICCPh) have been successfully incorporated into the large rigid core tetrameric frameworks. We also note that the adequate interpretation of the associated NMR structural characterization data of these large PDI assemblies can be quite challenging due to the substantial broadening of ^{1}H resonances (at RT) and is oftentimes overlooked in the literature. In some cases, it was argued that oligomeric PDIs exhibit such behavior as a result of aggregation-induced effects occurring at the typical NMR sample concentrations (mM range).[46] To fully address these questions, dynamic NMR experiments as well as concentration-dependent NMR studies have been performed to understand the origin of observed spectral broadening associated with single temperature (295 K) ^{1}H NMR experiments in the target PDI tetramers **1** and **2**.[29,47,48]

2. Results and discussion

2.1. Synthesis

The monomeric PDI precursors (**PDI** and **PDIBr**) were synthesized via modified literature procedures and the representative synthetic methodology is presented as Supplementary data in Scheme S1.[49,50] In general, the symmetric 1-hexylheptylamine was obtained in 95% yield via a facile reductive amination of commercially available dihexylketone in the presence of $NaBH_3CN$. In the next step, 1-hexylheptylamine was condensed under ambient conditions with commercially available 3,4,9,10-perylene-tetracarboxylic dianhydride (**PDA**) to obtain the corresponding perylenediimide (**PDI**) in a nearly quantitative yield (95%). **PDI** was then selectively brominated in the 1-position of its bay region with elemental Br_2 to afford 1-bromoperylenediimide (**PDIBr**) in 65% yield. Subsequently, **PDIBr** was used as a departure point to gain access to the target PDI tetramers **1** and **2** (Schemes 1 and 2), as well as the model monomer **3** (Scheme S1). Monomer **3** was obtained via a standard Sonogashira cross-coupling protocol of **PDIBr** with



1

2

3

Fig. 1. Structures of tetrahedral rigid core perylenediimide (PDI) tetramers and a model monomer: methane-centered PDI tetramer **1** (red), adamantane-centered PDI tetramer **2** (blue), and PDICCPh **3** (green). ***R*** denotes a hexyl (C_6H_{13}) group.