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Title:	Metal-free FRET macrocycles of perylenediimide and aza-BODIPY for multifunctional sensing.
Authors:	Rania, Kavita (/jspui/browse?type=author&value=Rania%2C+Kavita) Sengupta, Sanchita (/jspui/browse?type=author&value=Sengupta%2C+Sanchita)
Keywords:	Metal-free FRET macrocycles perylenediimide and aza-BODIPY multifunctional sensing
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Abstract:	<p>Two multichromophoric FRET macrocycles M1 [1+1] and M2 [2+2] with red emission (<math>\lambda_{em} \sim 721</math> nm) composed of perylenediimide (PDI) as the energy donor and aza-BODIPY (ABDP) as the energy acceptor were synthesized by click reaction in a metal-free fashion. M1 and M2 exhibited distinct reversible ratiometric temperature responsive emission with temperature sensitivities of 0.09–0.14% °C<sup>-1</sup> and owing to the redox active chromophores, they showed solution phase redox responsive reversible colour changes. Graphical abstract: Metal-free FRET macrocycles of perylenediimide and aza-BODIPY for multifunctional sensing</p> <p>Design and utilization of macrocyclic structures or assemblies for artificial light-harvesting (LH) have been of intense interest since the discovery of the circular bacteriochlorophyll dye arrangements and assemblies in natural LH systems of purple bacteria.<sup>1–4</sup> Macrocycles have been synthesized through covalent as well as non-covalent supramolecular strategies such as metal–ligand coordination, <math>\pi</math>–<math>\pi</math> stacking, and hydrogen bonding.<sup>5–9</sup> the latter strategies being more preferred as they overcome the challenges of multistep covalent synthesis. However, transition metal coordination may occasionally quench the emission of the chromophores due to coordination, the heavy atom effect or the formation of charge transfer complexes. Furthermore, a noble or transition metal-free approach is desirable to ensure sustainability and to keep the macrocycles emissive such that their fluorescence properties could be exploited for emergent functions, and metal-free macrocycles are thus of great interest. Furthermore, it is vital to develop stable covalent macrocycles that provide more robust frameworks compared to dynamic supramolecular systems.<sup>10</sup> Hence, some identified challenges in the realm of chromophore-based macrocycles are an efficient synthesis route for metal-free multichromophoric biomimetic macrocycles, precise spatial disposition of constituent chromophores and their optical complementarity for efficient Förster resonance energy transfer (FRET). Examples of metal-free covalent macrocycles containing different type of chromophores as LH FRET systems are rather limited in the literature,<sup>11</sup> and include the [1+1] macrocycle of naphthalenediimide (NDI),<sup>12</sup> a DAPPBox4+ [1+1] cycle of viologen and diazaperopyrenium.<sup>13</sup> Macrocyclic [1+1] dyads of PDI and fullerene are also studied for the photoinduced energy transfer processes<sup>14</sup> and intramolecular energy transfer within a [1+1] BINOL-perylene heterocycle has been reported recently.</p>
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