A Cyclophane–based Supramolecular Mechanophore that Shows Ratiometric Change in Emission Between Monomer and Exciplex

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The mechanophores are the molecular units that show various responses when an external mechanical force is applied.[1] The number of supramolecular mechanophores, in which the activation does not require covalent bond scission, is still limited.[2–4] Here, we report a cyclophane-based supramolecular mechanophore **1** featuring a 1,6–bis(phenylethynyl)pyrene luminophore and a pyromellitic diimide quencher. A linear reference compound **2** having the same luminophore and quencher was also synthesized. The monomer emission of the luminophore in cyclophane **1** is almost completely quenched in chloroform and toluene. In contrast, compound **2** shows partial quenching of the monomer emission from the luminophore. The cyclophane exhibits clear exciplex emission in toluene. Both the exciplex formation and effective quenching of the monomer emission in cyclophane are ascribed to the intramolecular charge–transfer interactions of the luminophore and quencher due to their close vicinity in the cyclic structure. Cyclophane **1** was covalently integrated into a linear segmented polyurethane to acquire **1-PU**. The **1-PU** films which were obtained through solvent casting exhibit exciplex–dominated orange emission. The deformation of the films results in changes of emission intensity ratio between monomer to exciplex, which is attributed to the spatial separation of the luminophore and the quencher. The changes in the emission intensity ratio show a correlation with the applied stress to the polymer film. The mechanochromic luminescence properties of the **1-PU** films is instantly reversible.

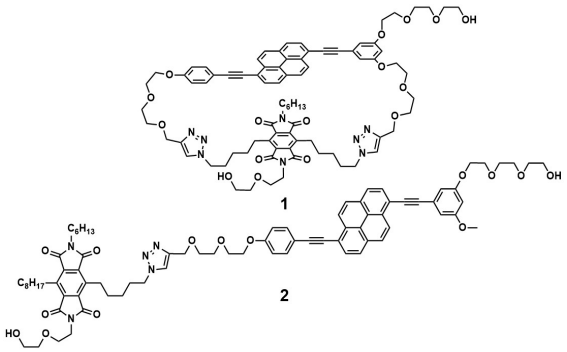

Fig. 1. Molecular structures of cyclophane **1** and linear reference compound **2**.

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