

Fluorescence switching with bisphosphonium

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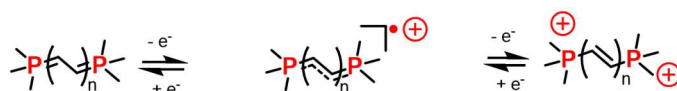
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Organic multi-stage redox systems are key component in many technological fields ranging from organic electronic (solar cells, batteries...) to spintronic. Among the strategies used to design such compounds, one approach consists in linking two cationic heteroatoms through a π -conjugated backbone featuring an even number of sp^2 C-atoms.¹ This led to the preparation of “Weitz type” derivatives with three stable redox states including a stable radical cation intermediate. Methylviologens (MV) are probably the most emblematic electron acceptors of this family.² Although Hünig *et al.* mentioned the applicability of this general strategy to systems in which phosphorus is the unique heteroatom (see Fig.), such derivatives were been described yet to the best of our knowledge, despite the wide literature on organophosphorus based π -systems and switches. To tackle this challenge, we here take advantage of the possibility to convert a cationic $\sigma^4\lambda^4 P^+$ -atom into a neutral $\sigma^4\lambda^5 P$ (Fig.) to afford multi-stage redox systems based on organophosphorus derivatives. Indeed we report the straightforward synthesis of an unprecedented family of dicationic P-containing Polycyclic Aromatic Hydrocarbons (PAHs) where two $\sigma^4\lambda^4 P^+$ atoms are connected through various PAH backbones. The effect of π -extension on both the optical and redox properties is investigated using a joint experimental/theoretical approach. Spectroelectrochemical studies prove that these compounds possess three stable redox states and EPR studies confirms the *in situ* formation of radicals demonstrating that these novel acceptors possess a “viologens-like” redox behaviour. Finally, electrochemical modulation of fluorescence performed on two compounds highlights the potential of these intrinsically switchable electroactive fluorophores.³



Intrinsically switchable electroactive fluorophores



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[2] Striepe, L.; Baumgartner, T. *Chem. Eur. J.* **2017**, 23, 16924-16940; Fang, L.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Goddard Iii, W. A.; Stoddart, J. F., *Chem. Soc. Rev.* **2010**, 39, 17-29.

[3](a)Delouche, T. ; Vacher, A. ; Caytan, E. ; Roisnel, T. ; Le Guennic, B. ; Jacquemin, D. ; Hissler, M. ; Bouit, P.-A. *Chem. Eur. J.* **2020**, 26, 8226. (b) Delouche, T. ; Vacher, A. ; Roisnel, T. ; Cordier, M. ; Audibert, J.-F. ; Le Guennic, B., Miomandre, F. ; Jacquemin, D. ; Hissler, M. ; Bouit, P.-A., *Mater. Adv* **2020**, 3369