ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2021, **57**, 2931

Received 18th January 2021,
Accepted 9th February 2021

DOI: 10.1039/d1cc00310k

rsc.li/chemcomm

Fine-tuning of the optical output in a dual responsive catenane switch†

Yulin Deng,[a] Samuel Kin-Man Lai,[a] Linghui Kong[a] and Ho Yu Au-Yeung *[ab]

A [2]catenane switch where the intramolecular pyrene excimer emission can be controlled by orthogonal cation binding and solvent polarity change in various amplitudes and dynamic ranges is reported.

Catenanes and related mechanically interlocked molecules (MIMs) are attractive structural units for the construction of molecular switches, because the flexible and strong mechanical bond could enable the interlocked macrocycles to undergo large-amplitude intramolecular motions and switch between different states in response to a stimulus.[1,2] A common design strategy of a catenane switch is to have two or more co-conformations of considerable but different stabilities, where the application of a stimulus will enhance or disrupt the interactions at one recognition site, such that the relative stability of the co-conformations is reversed and a switching is resulted. Although co-conformation switching in MIMs has been well studied and can be achieved by using various kinds of stimuli,[2] most reports are primarily focused on the structural aspect of the switching process, where the stability of one of the co-conformations is modulated by a single stimulus in the switching process. On the other hand, engineering a desirable output to accompany the structural change is less straightforward because the co-conformational change will have to associate with a difference in the chemical and/or physical properties, and therefore a more elaborate way to control the relative stability of the co-conformations is necessary if a specific output is to be generated.[3]

Instead of effecting the switching by altering the stability of one of the co-conformations, decoupling the signal generation into separate processes such that the stability of each co-conformation is controlled by an individual stimulus will offer additional mechanisms in modulating the relative stability of the co-conformations, and hence more elaborate control over the associated output can be realised.[4] In this work, a pyrene-functionalised [2]catenane switch responsive to both cation binding and solvent polarity change is reported (Fig. 1a). Specifically, cation binding is employed to lock/unlock the interlocked macrocycles from large-amplitude co-conformational change, whereas a change in solvent polarity is used to fine tune the intramolecular pyrene–pyrene distance to effect an excimer emission (Scheme 1). Compared with other MIMs that are switched by one kind of stimulus, the dual responsiveness will allow more flexible and versatile control over the relative stability of the catenane co-conformations, and the amplitude of the luminescent output can be controlled in a progressive fashion with the orthogonal stimuli.

The [2]catenane switch **1** contains two interlocked, phenanthroline-derived macrocycles that are appended with a pyrene (Fig. 1b). When a cation binds to the interlocked phenanthrolines, rotatory motions of the interlocked macrocycles will be "locked".

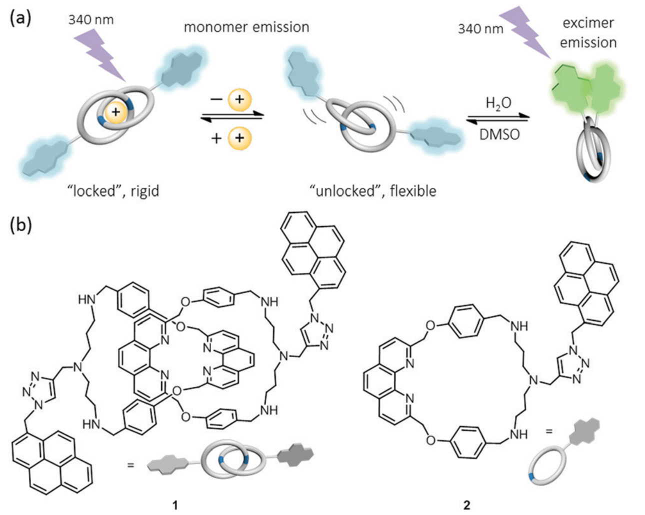


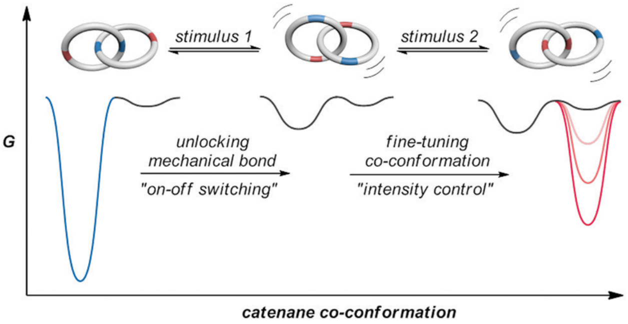
Fig. 1 (a) Cation (un)locks **1** from large-amplitude co-conformational change and hydrophobic interactions fine tune the intramolecular pyrene distance. (b) Molecular structure of [2]catenane **1** and the control compound **2**.

---

[a] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. E-mail: hoyuay@hku.hk*

[b] *State Key Laboratory of Synthetic Chemistry and CAS-HKU Joint Laboratory of Metallomics on Health and Environment, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China*

† Electronic supplementary information (ESI) available: Synthetic procedures, spectra and computation details. See DOI: 10.1039/d1cc00310k



Scheme 1 A dual responsive [2]catenane switch in which the (un)locking of the mechanical bond and co-conformational change are controlled by two orthogonal stimuli.

Since the pyrene is attached onto the macrocycle at a point that is farthest away from the phenanthroline, the pyrenes will be kept from being in close proximity and no emission from intramolecular pyrene excimer will occur.[5] In the absence of the cation, **1** will be in an "unlocked" state and co-conformational changes are unrestricted. An increase in the water content in the solvent will enhance the hydrophobic interactions between the two pyrenes and favour the formation of an intramolecular pyrene excimer with a new excimer emission.[6] Synthesis of **1** is straightforward with a templated catenane formation, followed by a click modification that appended the pyrenes (see the ESI,† for details).

A DMSO solution of **1** is light yellow and the UV-Vis spectrum shows strong pyrene absorptions at 334 nm, ε = 32 000 M^{-1} cm^{-1} and 351 nm, ε = 34 800 M^{-1} cm^{-1} (Fig. S1, ESI†). Photoexcitation (λ_{ex} = 340 nm) of a 25 μM solution of **1** in DMSO showed two emission peaks at 378 nm and 398 nm which are characteristic of non-aggregated pyrene (Fig. 2a).[7] There is also a broad and weak emission at 485 nm that can be assigned as the emission from a pyrene excimer, suggesting that the mechanical bond in **1** is flexible and that the [2]catenane switch can adopt a co-conformation that favours excimer formation.[7] Upon increasing the solvent polarity by introducing water as a co-solvent, a significant increase in the emission intensity at 485 nm (I_{485}) was observed when the water percentage was above 50%. A 13-fold enhancement of I_{485} was resulted when the water content is 90% when compared with that of **1** in pure DMSO. In addition, a 50 μM solution of the non-interlocked monomer **2** in DMSO showed no emission at 485 nm, confirming that the excimer emission from **1** is intramolecular in nature and that **1** is co-conformationally flexible and responsive to a change in solvent polarity.

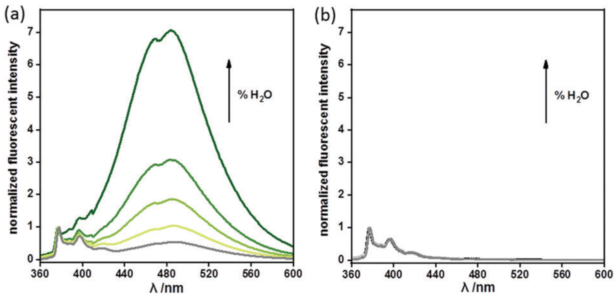


Fig. 2 Normalised emission spectra of a 25 μM solution of (a) **1** (unlocked state) and (b) $[Zn(\mathbf{1})]^{2+}$ (locked state) in DMSO with an increasing amount of water (0%, 60%, 70%, 80% and 90%).

As the pyrene excimer emission from **1** is premised on the flexibility of the [2]catenane to form an intramolecular pyrene excimer, rigidifying the mechanical bond in **1** could disable the solvent-induced switching of the excimer emission. By coordinating the phenanthrolines in **1** to a Zn^{2+} ion, the $[Zn(\mathbf{1})]^{2+}$ complex is formed (see the ESI†). In addition, the phenyl linkers also π-stack with the phenanthrolines as supported by an upfield shift of 0.3–0.8 ppm for the phenyl protons in the ^{1}H NMR spectrum of $[Zn(\mathbf{1})]^{2+}$ when compared to that of **1** (Fig. S37, ESI†). Such π-stacking will further rigidify the mechanical bond and limit the co-conformational flexibility of the [2]catenane switch.[8] Consistent with the rigid structure, no intramolecular pyrene excimer was formed and no emission at 485 nm was observed from a 25 μM solution of $[Zn(\mathbf{1})]^{2+}$ in water/DMSO of all tested ratios (Fig. 2b). The fluorescent output from the [2]catenane switch was therefore effectively turned-off in the "locked" state upon coordination to a Zn^{2+} ion.

Co-conformational flexibility of the [2]catenane switch in the "locked" and "unlocked" states was also studied by molecular dynamics (MD) simulations on **1** and $[Zn(\mathbf{1})]^{2+}$ in DMSO and water (Fig. 3). Consistent with the tetrahedral coordination geometry, the angle between the phenanthroline planes (α) in $[Zn(\mathbf{1})]^{2+}$ was found to be consistently about 87° with a distance of 7.1 Å between the centroids of the two phenanthrolines (d) in both DMSO and water (Fig. S13 and S14, ESI†). The two pyrenes were also found to be separated by ∼25 Å which is too distant for efficient excimer formation. These observations agree well with the mechanical bond being locked by the Zn^{2+} ion and the observation that the excimer fluorescence was completely turned off in the "locked" state. In contrast, MD simulations on **1** showed

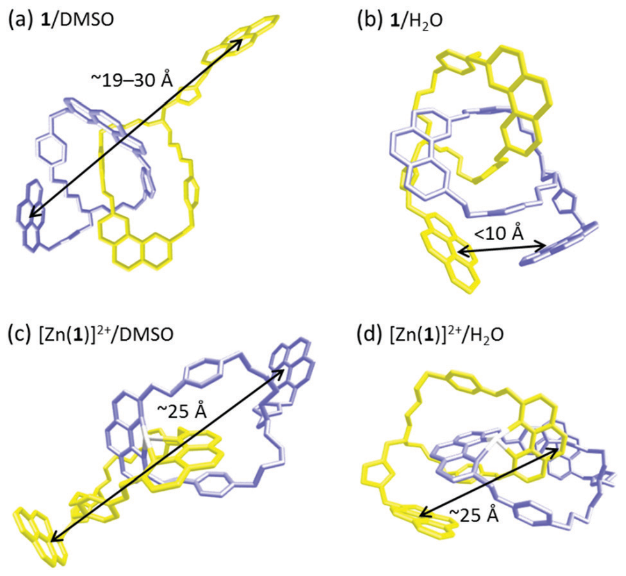


Fig. 3 Representative structures of **1** in (a) DMSO and (b) water, and $[Zn(\mathbf{1})]^{2+}$ in (c) DMSO and (d) water obtained using MD simulations.

a more rapid relative oscillation of both α (from 74° to 105°) and d (from 7.3 Å to 13.7 Å) in water. Similar fluctuations in α and d were also observed when the dynamics of **1** were simulated in DMSO, consistent with the [2]catenane switch being in the "unlocked" state with a more flexible mechanical bond. The averaged distance between the two pyrenes in **1** is different in the two solvents. In DMSO, the distance between the two pyrenes was found to vary between 19.1 Å and 30.2 Å, but an average pyrene–pyrene distance of $<$10 Å, which will allow the formation of pyrene excimer, was found in water.[9] Compared with most other phenanthroline-based [2]catenanes in which the switching is effected only by cation (un)binding,[10] the use of two stimuli to effect the co-conformational switching is advantageous as the relative stability of the co-conformations, and hence amplitude of the output, can be fine-tuned by a specific combination of the two stimuli.

In the co-conformational switching of **1**, on–off control of the excimer emission is achieved by cation (un)binding and the excimer emission intensity is controlled by the solvent polarity. Due to the strong Zn^{2+}-phenanthroline coordination ($\log K \approx 12$),[11] locking of the catenane switch in the "off" state is very efficient and the use of 1 equiv. of Zn^{2+} ions is sufficient to completely switch off the excimer emission. By using other cations of different binding strengths to bind to the phenanthrolines in **1**, the dynamic range of the polarity-controlled luminescent signal can be modulated. For example, locking the mechanical bond in **1** using 1 equiv. of Cu^+, which is known to bind strongly to phenanthroline-based catenane,[10,12] resulted in a similar switching as that of using Zn^{2+} and no pyrene excimer emission at 485 nm was observed in 90% water/DMSO (Fig. S6, ESI†). The use of weaker binding s-block metals,[12a,13] on the other hand, resulted only in a partial suppression of the polarity-induced excimer emission. For example, I_{485} of **1** in 90% water/DMSO was found to be reduced by ~11%, ~5% and ~18% when 1 equiv. of Li^+, Na^+ and Ca^{2+} was introduced respectively (Fig. 4).[14] Furthermore, the dynamic range of the polarity-dependent excimer emission can also be tuned by using different amounts of the s-block metals. For example, I_{485} of **1** in 90% water/DMSO was found to be reduced by 43% and 80% in the presence of 10 equiv. and 100 equiv. of Na^+ respectively. It is worth noting that in most metal-based MIM switches, metals that optimally satisfy the coordination properties at the recognition sites are commonly used to effect the switching to a maximum extent.[15] Yet, with the present dual switching where the output is dependent on two inputs, metal ions that are weaker binding with a "mismatch" in the coordination properties (*i.e.* hard $Li^+/Na^+/Ca^{2+}$ with the borderline, N-based phenanthrolines in a tetrahedral geometry) could also be advantageously used to fine-tune the amplitude and dynamic range of the output, thus making the [2]catenane much more versatile with diverse ways of control and amplitude settings.

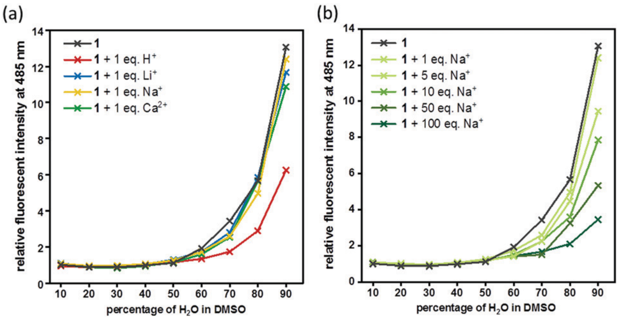


Fig. 4 Relative emission intensity at 485 nm of **1** in the presence of (a) 1 equiv. of various cations and (b) increasing amount of Na^+ in DMSO with an increasing amount of water (10% to 90%).

Finally, locking of the mechanical bond in **1** by acid has also been studied. [2]Catenanes with two phenanthrolines similar to **1** have been previously reported to bind to a proton and the phenanthrolines are held in the core of the [2]catenane in the resulting acid–base adduct.[10b,c,16] In our study, addition of 1 equiv. of trifluoroacetic acid to **1** in 90% water/DMSO resulted in a decrease of I_{485} by 56%, suggesting that the phenanthrolines in **1** were locked in the centre of the [2]catenane and formation of the intramolecular pyrene excimer was disfavoured.[17] MD simulation on the monoprotonated $[(\mathbf{1})H]^+$ also showed that the two pyrenes are separated by ~15 Å which is slightly too long for the intramolecular pyrene excimer formation (Fig. S15 and S16, ESI†). A representative structure of $[(\mathbf{1})H]^+$ also showed that the two phenanthrolines are locked in the [2]catenane core with structural parameters comparable to that of a published crystal structure of a monoprotonated phenanthroline-containing [2]catenane,[16a] showing that the flexibility of the mechanical bond in **1** can also be controlled by acid–base chemistry (see the ESI,† for details).

In summary, a simple [2]catenane switch with a two-stage control of the intramolecular excimer fluorescence is reported. While the proximity of the pyrenes is dependent on the strength of the hydrophobic interactions in solvents of different polarity, flexibility of the mechanical bond for the pyrenes to approach each other is controlled by the presence of a cation that locks the phenanthrolines. A range of cations can be used to lock the mechanical bond in **1** in different degrees and the pyrene excimer fluorescence can therefore be versatilely controlled by various stimuli including solvent polarity, transition metals, main group metals and proton. With two orthogonal inputs to generate a luminescent output, the [2]catenane switch can also be considered as a molecular logic gate for applications such as molecular keypad locks in which a signal is generated by a correct combination of inputs in a specific sequence.[18]

This work was supported by the Croucher Foundation. We acknowledge UGC funding administered by The University of Hong Kong for support of the Electrospray Ionization Quadrupole Time-of-Flight Mass Spectrometry Facilities under the support for Interdisciplinary Research in Chemical Science.

Conflicts of interest

There are no conflicts to declare.

References

1 (*a*) J.-P. Collin, J. M. Kern, L. Raehm and J.-P. Sauvage in *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001, ch. 8, pp. 249–280; (*b*) V. Balzani, M. Gomez-Lopez and J. F. Stoddart, *Acc. Chem. Res.*, 1998, **31**, 405; (*c*) S. Kassem, T. van Leeuwen, A. S. Lubbe, M. R. Wilson,

B. L. Feringa and D. A. Leigh, *Chem. Soc. Rev.*, 2017, **46**, 2592; (*d*) M. Baroncini, L. Casimiro, C. de Vet, J. Groppi, S. Silvi and A. Credi, *ChemistryOpen*, 2018, **7**, 169; (*e*) W. Yang, Y. Li, H. Liu, L. Chi and Y. Li, *Small*, 2012, **8**, 504; (*f*) J. J. Davis, G. A. Orlowski, H. Raman and P. D. Beer, *Chem. Commun.*, 2010, **46**, 54; (*g*) J. P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611; (*h*) H. Liang, B. Hua, F. Xu, L.-S. Gan, L. Shao and F. Huang, *J. Am. Chem. Soc.*, 2020, **142**, 19772; (*i*) H. Xing, Z. Li, W. Wang, P. Liu, J. Liu, Y. Song, L. Wu Zi, W. Zhang and F. Huang, *CCS Chem.*, 2020, **2**, 513; (*j*) H. Xing, Z. Li, Z. L. Wu and F. Huang, *Macromol. Rapid Commun.*, 2018, **39**, 1700361.

2 (*a*) C. J. Bruns and J. F. Stoddart, *The Nature of Mechanical Bond: from Molecules to Machines*, John Wiley & Sons, New Jersey, 2017, ch. 6, pp. 555–707; (*b*) G. Gil-Ramírez, D. A. Leigh and A. J. Stephens, *Angew. Chem., Int. Ed.*, 2015, **54**, 6110.

3 For examples of catenane-based optical switches: (*a*) Y. Zhang, Q. Chen, Y. Wang, X. Zheng, H. Wang, F. Cao, A. C.-H. Sue and H. Li, *Chem. Commun.*, 2020, **56**, 11887; (*b*) J. Sun, Y. Wu, Y. Wang, Z. Liu, C. Cheng, K. J. Hartlieb, M. R. Wasielewski and J. F. Stoddart, *J. Am. Chem. Soc.*, 2015, **137**, 13484; (*c*) C.-Y. Tsai, C.-C. Lai, Y.-H. Liu, S.-M. Peng, R. P. Cheng and S.-H. Chiu, *J. Org. Chem.*, 2018, **83**, 5619.

4 (*a*) D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174; (*b*) J. V. Hernández, E. R. Kay and D. A. Leigh, *Science*, 2004, **306**, 1532; (*c*) W. Zhou, J. Li, X. He, C. Li, J. Lv, Y. Li, S. Wang, H. Liu and D. Zhu, *Chem. – Eur. J.*, 2008, **14**, 754; (*d*) Y.-C. You, M.-C. Tzeng, C.-C. Lai and S.-H. Chiu, *Org. Lett.*, 2012, **14**, 1046; (*e*) Z. Meng, J.-F. Xiang and C.-F. Chen, *Chem. Sci.*, 2014, **5**, 1520.

5 (*a*) S. Karuppannan and J.-C. Chambron, *Chem. – Asian J.*, 2011, **6**, 964; (*b*) X.-Q. Wang, Q.-H. Ling, W. Wang and L. Xu, *Mater. Chem. Front.*, 2020, **4**, 3190.

6 For examples of polarity-driven switching: (*a*) K. Yamauchi, A. Miyawaki, Y. Takashima, H. Yamaguchi and A. Harada, *J. Org. Chem.*, 2010, **75**, 1040; (*b*) S. Dong, J. Yuan and F. Huang, *Chem. Sci.*, 2014, **5**, 247; (*c*) T. A. Barendt, L. Ferreira, I. Marques, V. Félix and P. D. Beer, *J. Am. Chem. Soc.*, 2017, **139**, 90260.

7 (*a*) T. Förster, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 333; (*b*) J. B. Birks, *Rep. Prog. Phys.*, 1975, **38**, 903; (*c*) F. M. Winnik, *Chem. Rev.*, 1993, **93**, 587.

8 K. Wang, C.-C. Yee and H. Y. Au-Yeung, *Chem. Sci.*, 2016, **7**, 2787.

9 (*a*) J. B. Birks, *Photophysics of aromatic molecules*, Wiley-Interscience, New York, 1970; (*b*) G. K. Bains, S. H. Kim, E. J. Sorin and V. Narayanaswami, *Biochemistry*, 2012, **51**, 6207.

10 (*a*) M. Cesario, C. O. Dietrich-Buchecker, J. Guilhem, C. Pascard and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1985, 244; (*b*) D. B. Amabilino, C. O. Dietrich-Buchecker, A. Livoreil, L. Pérez-García, J.-P. Sauvage and J. F. Stoddart, *J. Am. Chem. Soc.*, 1996, **118**, 3905; (*c*) J. A. Berrocal, C. Biagini, L. Mandolini and S. Di Stefano, *Angew. Chem., Int. Ed.*, 2016, **55**, 6997; (*d*) C. Biagini, S. Albano, R. Caruso, L. Mandolini, J. A. Berrocal and S. Di Stefano, *Chem. Sci.*, 2018, **9**, 181; (*e*) L. Zhu, J. Li, J. Yang and H. Y. Au-Yeung, *Chem. Sci.*, 2020, **11**, 13008.

11 C. V. Banks and R. I. Bystroff, *J. Am. Chem. Soc.*, 1959, **81**, 6153.

12 (*a*) C. O. Dietrich-Buchecker, J. P. Sauvage and J. M. Kern, *J. Am. Chem. Soc.*, 1984, **106**, 3043; (*b*) A.-M. Albrecht-Gary, Z. Saad, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1985, **107**, 3205; (*c*) C. O. Dietrich-Buchecker, J.-P. Sauvage and J.-M. Kern, *J. Am. Chem. Soc.*, 1989, **111**, 7791; (*d*) J. A. Berrocal, M. M. L. Nieuwenhuizen, L. Mandolini, E. W. Meijer and S. Di Stefano, *Org. Biomol. Chem.*, 2014, **12**, 6167; (*e*) K.-L. Tong, C.-C. Yee, Y. C. Tse and H. Y. Au-Yeung, *Inorg. Chem. Front.*, 2016, **3**, 348.

13 (*a*) N. Armaroli, L. De Cola, V. Balzani, J.-P. Sauvage, C. O. Dietrich-Buchecker, J.-M. Kern and A. Bailal, *J. Chem. Soc., Dalton Trans.*, 1993, 3241; (*b*) C. Dietrich-Buchecker and J.-P. Sauvage, *Chem. Commun.*, 1999, 615.

14 Binding constants of **1** to Li^+, Na^+ and Ca^{2+} obtained by flurorescence titration are 7200 M^{-1}, 7300 M^{-1} and 9600 M^{-1} respectively; see ESI† for details.

15 (*a*) B. Champin, P. Mobian and J.-P. Sauvage, *Chem. Soc. Rev.*, 2007, **36**, 358; (*b*) S. Durot, F. Reviriego and J.-P. Sauvage, *Dalton Trans.*, 2010, **39**, 10557; (*c*) J. E. Beves, A. A. Blight, C. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem., Int. Ed.*, 2011, **50**, 9260; (*d*) W.-X. Gao, H.-J. Feng, B.-B. Guo, Y. Lu and G.-X. Jin, *Chem. Rev.*, 2020, **120**, 6288.

16 (*a*) M. Cesario, C. O. Dietrich, A. Edel, J. Guilhem, J. P. Kintzinger, C. Pascard and J. P. Sauvage, *J. Am. Chem. Soc.*, 1986, **108**, 6250; (*b*) C. Biagini, F. Di Pietri, L. Mandolini, O. Lanzalunga and S. Di Stefano, *Chem. – Eur. J.*, 2018, **24**, 10122.

17 For the complex acid-base equilibria involving multiple basic nitrogens in **1**, and because protonation near the pyrene may also affect its emission, pK_a measured from fluorescence titration of **1** may not reliably reflect the basicity of **1**. See ESI† for details.

18 J. Andreasson and U. Pischel, *Chem. Soc. Rev.*, 2018, **47**, 2266.