Alcohol- and acid-causing reversible switching of near-infrared absorption and luminescence in a donor–acceptor conjugated system†

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2-Substituted 7-oxo-7,11b-dihydrodibenzochromenilium derivatives (1-ArPyl$^+$s) undergo reversible changes in near-infrared absorption when Ar = ferrocenyl, and complete on–off switching of luminescence when Ar = *p*-tolyl, *m*-tolyl, or phenyl, by the reaction with methanol or methoxide ion and with acid.

New molecules that reversibly change their chemical and/or physical properties in response to external stimuli have received significant attention because of their potential versatility in applications related to molecular memory and switches.[1–5] Donor–acceptor (D–A) conjugated molecules are candidates for these purposes; determining the mechanism of switching in the D–A interaction is the key issue in achieving bistability which implies that a molecule can be resting in two states. We previously studied a series of donor–acceptor complexes, ferrocenylethynylanthraquinones (FcAqs),[6,7] and recently reported novel protonation-induced cyclocondensation reactions of 1-arylethynylanthraquinones (1-ArAqs), which produce tetracyclic compounds containing a pyrylium ring (1-ArPyl$^+$), expanding the π-conjugated system and displaying a strong red color.[8] This change occurs when the lowest unoccupied molecular orbital (LUMO) level is lowered in the protonated species. When the aryl group was the strong donor ferrocene (1-FcAq), an intervalence charge transfer (IVCT) band appeared and a temperature-dependent change in the valence state was observed with the valence tautomerization (VT) that resulted when the LUMO level was lowered by the expansion of the π-conjugation system of the acceptor moiety, which led in turn to a strong donor–acceptor interaction (Fig. 1). These compounds constitute a new class of π-conjugated molecules, the properties of which can be controlled by the degree of donor–acceptor interaction.

In this study, we aimed to control the π-conjugation structure (which is closely associated with the LUMO level of 1-ArPyl$^+$) *via* chemical stimuli to produce a remarkable molecular switching system. We found that the π-conjugated structure of 1-ArPyl$^+$ is abolished by the addition of methanol and is regenerated by the addition of acid. This reversible structural change causes complete on–off switching in the appearance of the IVCT band of the ferrocenyl derivative and in the luminescent properties of the tolyl and phenyl derivatives. These reversible structural changes have not previously been observed in monocyclic pyrylium compounds.

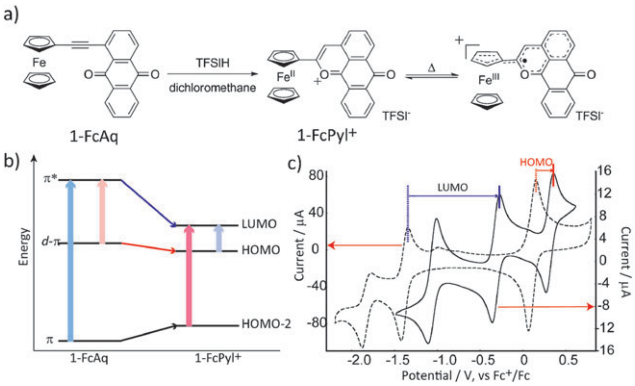

Fig. 1 Protonation-induced cyclocondensation of 1-FcAq to produce 1-FcPyl$^+$ and the valence tautomerization of 1-FcPyl$^+$. (a) Changes in the chemical structure. (b) Energy diagram for 1-FcAq and 1-FcPyl$^+$. (c) Cyclic voltammograms of 1-FcAq (dotted line) and 1-FcPyl$^+$TFSI$^-$ (solid line) in 0.1 M Bu_4NClO_4–CH_2Cl_2 at 0.1 V s^{-1}.

A series of 1-ArPyl$^+$TFSI$^-$ (Ar = *p*-Tol, *m*-Tol, Ph, or Fc) was synthesized by the cyclocondensation reaction of 1-ArAqs with 1.5 eq. of bis(trifluoromethanesulfone)imide (TFSIH), as reported previously.[8] In aprotic solvents, the 1-ArPyl$^+$ ions exhibited a π–π* band around 500 nm, indicating the presence of a large π-conjugated system, whereas this band was completely lost in protic organic solvents, such as methanol, ethanol, and isopropanol (see Fig. S1, ESI†). Pyrylium compounds show ring opening/closing reactions in response to base–acid stimuli,[9–11] in which the ring opening of the pyrylium moiety completely destroys the aromaticity of the ring. Therefore, it is expected that 1-ArPyl$^+$ undergoes a neutralization reaction with alcohol, leading to the loss of the aromaticity of the pyrylium ring. To confirm this assumption, 1-*p*-TolPyl$^+$ was reacted with a base, NaOMe. The reaction was performed by the addition of excess NaOMe to a dichloromethane solution of 1-*p*-TolPyl$^+$. The UV–Vis absorption spectrum of the isolated product agreed completely with that of 1-*p*-TolPyl$^+$ in methanol (see Fig. S2, ESI†). In an ^{1}H nuclear magnetic resonance (NMR) spectrum of the isolated compound in MeCN-d_3 (Fig. 2 and S3, ESI†), a new peak was observed at 3.00 ppm, which was assignable

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† Electronic supplementary information (ESI) available: Details in determination of the structure of 1-*p*-TolPyl-OMe, experimental and calculated excitation energies to the lowest excited state for 1-*p*-TolPyl-OMe (Table S1), UV-Vis spectra of 1-*p*-TolPyl in different solvents (Fig. S1), UV-Vis spectra of 1-*p*-TolPyl in methanol and the isolated compound in reaction of 1-*p*-TolPyl and NaOMe, a ^{1}H NMR spectrum of 1-*p*-TolPyl-OMe (Fig. S3), the optimized molecular structure of 1-*p*-TolPyl-OMe (Fig. S4), molecular orbitals of 1-*p*-TolPyl-OMe (Fig. S5), UV-Vis-NIR spectra of 1-ArPyl$^+$ (Fig. S6), and the changes of absorbance at 536 nm of a 1-*p*-TolPyl$^+$ solution upon the alternate addition of TBACl and TFSIH (Fig. S7). See DOI: 10.1039/b823248b

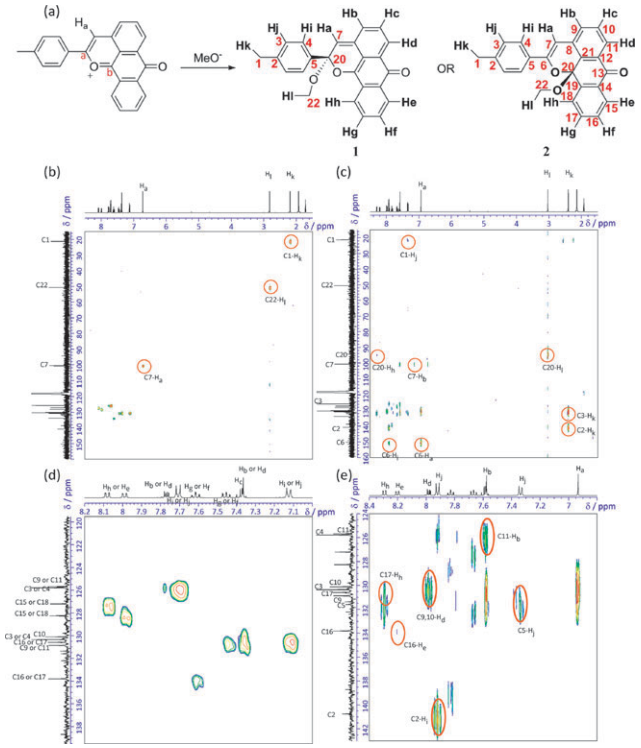

Fig. 2 ^{1}H NMR spectra of 1-*p*-TolPyl-OMe in acetonitrile-d_3. (a) Chemical structures of **1** and **2**. HMQC (b) and HMBC (c) spectra and their enlarged spectra for (d) and (e), respectively.

to a methoxy group. The molar ratio of the methoxy group to 1-*p*-TolPyl$^+$ was 1 : 1. An upfield shift of H_a of the pyrylium ring was also observed, supporting the disappearance of the π-conjugated system of the pyrylium moiety. With these results, we confirmed the progression of the neutralization reaction, which formed only one product. As shown in Fig. 2, the 2 and 6 positions of the pyrylium ring underwent nucleophilic attack by the base and the ring-opening reaction proceeded.[2] In the case of 1-*p*-TolPyl$^+$, which has an asymmetric pyrylium ring, a methoxide ion can attack both C_a and C_b; consequently, two structures of the product are possible, **1** and **2**, as shown in Fig. 2. With heteronuclear multiple-bond correlation (HMBC) measurements, a cross peak between H_a and C_a was observed, and the chemical structure of the isolated compound was thus determined to be **2** in Fig. 2 (for details, see ESI†). Thus, 1-RPyl$^+$ completely lost the aromaticity of the pyrylium ring with the addition of the methoxide ion.

The contraction of the π-conjugated system was also supported by time-dependent density functional theory (TD-DFT) calculations using B3LYP/6-31G + (p,d) basis sets for all atoms (see the geometry of 1-*p*-TolPyl-OMe in Fig. S4, ESI†). 1-*p*-TolPyl-OMe showed a weak band at around 385 nm, assignable to the transition from the highest occupied molecular orbital (HOMO), consisting of the π-orbital extended in the *p*-tolyl moiety and the adjacent six-membered ring (see Fig. S5 and Table S1, ESI†), to LUMO, consisting of the π* orbital extended in the tricyclic moiety, and a strong band around 325 nm, which was assigned to the transition from HOMO to LUMO + 1, consisting of the π* orbital extended in the tricyclic moiety. Structure **2** indicates that the reaction of the 1-ArPyl$^+$s with base generates a base-adducted species instead of a ring-opened compound, unlike the monocyclic pyrylium salts. This is because the enol species is largely stabilized by the stilbene-like structure in 1-ArPyl-OMe, which prevents the ring-opening reaction.

We next studied the reversibility of the changes in physical properties caused by the alternation of the π-conjugated system between 1-ArPyl$^+$ and 1-ArPyl-OMe. As shown in Fig. 3(a), the ππ* band of the pyrylium ring disappeared with the stepwise addition of methanol to dichloromethane solutions of 1-ArPyls. All spectral changes exhibited isosbestic points indicating the absence of side reactions, producing solely 1-ArPyl-OMe. The further addition of TFSIH to the solution recovered the appearance of the ππ* band at 500 nm, with again the isosbestic points shown in Fig. 3(b), indicating the completely reversible change in chemical structure between 1-ArPyl$^+$ and 1-ArPyl-OMe.

It should be noted that the 1-ArPyl$^+$s, except 1-FcPyl$^+$, exhibit emission bands at around 600 nm (λ_{em} = 650 for Ar = *p*-Tol, 620 for *m*-Tol, and 600 nm for Ph) (Fig. 3(c)). The band shapes are mirror images of the π–π* absorption bands (see Fig. S6, ESI†) and the Stokes' shifts are about 100 nm, indicating that the emission is assignable to fluorescence from the S_1 excitation state. The fluorescence quantum yields of the 1-ArPyl$^+$s were determined to be 0.09 (*p*-Tol), 0.20 (*m*-Tol), and 0.19 (Ph) in dichloromethane at room temperature.[12]

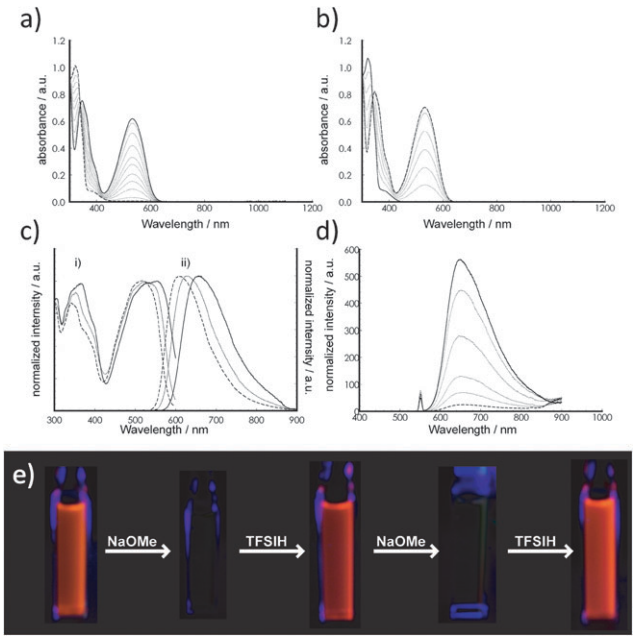

Fig. 3 Alcohol and acid responses of 1-ArPyl$^+$. (a) UV-Vis–NIR spectral changes in 1-*p*-TolPyl$^+$ with the addition of 0 (solid line) to 100 μL of methanol (dashed line). (b) UV-Vis–NIR spectral changes in 1-*p*-TolPyl-OMe with the addition of 0 (solid line) to 1 eq. of TFSIH (dashed line). (c) Excitation (i) and emission (ii) spectra of 1-*p*-TolPyl$^+$ (solid lines), 1-*m*-TolPyl$^+$ (dotted lines), and 1-PhPyl$^+$ (dashed lines) in dichloromethane at room temperature. (d) Changes in the emission spectra of 1-*p*-TolPyl$^+$ upon the addition of 0 (solid line) to 100 μL of methanol (dashed line). (e) Photographs of 1-PhPyl$^+$ in dichloromethane with 360 nm light irradiation with the alternate addition of excess NaOMe and TFSIH.

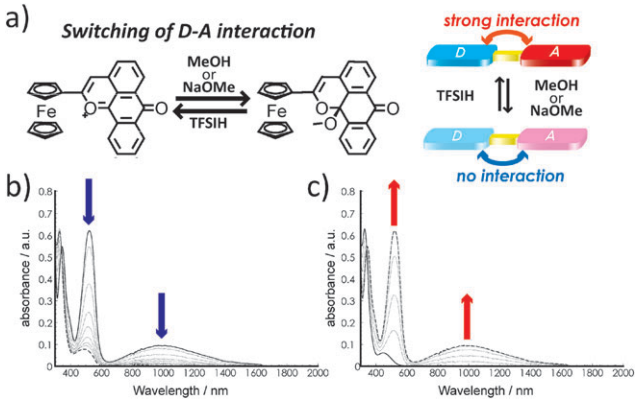

Fig. 4 Alcohol and acid responses of 1-FcPyl$^+$. (a) Switching of the D–A interaction between 1-FcPyl$^+$ and 1-FcPyl-OMe. (b) UV-Vis–NIR spectral changes in 1-FcPyl$^+$ upon the addition of 0 (solid line) to 80 μL methanol (dashed line). (c) UV-Vis–NIR spectral changes in 1-FcPyl-OMe upon the addition of 0 (solid line) to 1 eq. of TFSIH (dashed line).

As expected, these emissions of 1-ArPyl$^+$s in dichloromethane disappeared with the loss of π-conjugation with the stepwise addition of methanol, as shown in Fig. 3(d). No emission occurred in the solution with a sufficient amount of methanol. Repetitive additions of NaOMe and TFSIH caused the reversible and complete quenching and the recovery of the fluorescence of 1-PhPyl$^+$, as shown in Fig. 3(e).

No emission was observed for 1-FcPyl$^+$ because the ferrocene moiety acts as a strong emission quencher.[13,14] However, the absorption band around 1000 nm, assigned to the IVCT transition, responded to the addition of NaOMe and acid, causing a reversible change in the chemical structure between 1-FcPyl$^+$ and 1-FcPyl-OMe (Fig. 4a). Fig. 4b shows the changes in the UV-Vis–near-infrared (NIR) spectra with the stepwise addition of methanol to a solution of FcPyl$^+$TFSI$^-$ in dichloromethane, and Fig. 4c shows those spectra on the further addition of TFSI. Both figures give the isosbestic points and Fig. 4a shows the complete disappearance of the NIR band, indicating the complete change between FcPyl$^+$ and 1-FcPyl-OMe.

The reversible change in 1-ArPyl$^+$ with base–acid stimulation was also achieved with Bu_4NCl. The addition of a stoichiometric amount of Bu_4NCl (1.0 eq.) to a dichloromethane solution of 1-*p*-TolPyl$^+$ quantitatively formed a chloro-attached product, 1-*p*-TolPyl-Cl. This product was reconverted to 1-*p*-TolPyl$^+$ by the addition of a stoichiometric amount of TFSIH (1.0 eq.) (see Fig. S7, ESI†).

In conclusion, we have shown that 1-ArPyl$^+$ can be reversibly converted to 1-ArPyl-OMe and 1-ArPyl-Cl using bases and acids as external stimuli. Furthermore, the conversion causes a change in the π-conjugated system of the pyrylium ring, leading to a switching of the fluorescence properties of 1-*p*-TolPyl$^+$, 1-*m*-TolPyl$^+$, and 1-PhPyl$^+$, and IVCT absorption resulting from the change in the donor–acceptor interaction of 1-FcPyl$^+$.

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