

Electronic Supplementary Information

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

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Determination of the structure of **1-*p*-TolPyl-OMe**

The chemical structure of **1-*p*-TolPyl-OMe**, an acetal compound of **1-*p*-TolPyl**, was determined by ^1H NMR, ^{13}C NMR, HMQC, and HMBC spectra. In this section, the assignment of these spectra is described in detail.

^1H NMR, HMQC, and HMBC spectra of **1-*p*-TolPyl-OMe** are shown in Figs. 2 and S3. The expected chemical structures of **1-*p*-TolPyl-OMe** are shown in Fig. 2a. **1** and **2** can be distinguished by HMBC measurement, because carbon atoms that have correlation with H_a (see Fig. 2a) should change (i.e. H_a of **1** would correlate with C20 and, H_a of **2** would correlate with C6).

In the ^1H NMR spectrum, three peaks that are assignable to a proton of methyl group (H_k in Fig. 2a), that of a methoxy group (H_l), and H_a were observed at 2.41, 3.03, and 6.93 ppm, respectively. From the result of HMQC measurement, peaks of ^{13}C observed at 21.2, 50.6, and 100.7 ppm are assigned to C1, C22, and C7, respectively. In an HMBC spectrum, cross peaks between H_k and ^{13}C were observed at 130.3, and 140.7 ppm, and these peaks are assigned to C3 and C2, respectively. Thus, judging from the results of HMQC and HMBC measurement, peaks of ^1H observed at 7.34 and 7.92 ppm are assignable to H_j and H_i , respectively. The peak at 94.4 ppm is assigned to C20 because the peak had correlation with H_l . The cross peak between C20 and H_a was not observed in the HMBC spectrum. Moreover, C20 had correlation with H_h in the HMBC spectrum. From these reasons, it is indicated that the chemical structure of **1-*p*-TolPyl-OMe** is not **1** in Fig. 2a. On the other hand, the correlation between H_a and the peak at 150.4 ppm was observed in the HMBC spectrum. The peak at 150.4 ppm also had correlation with H_i in the HMBC spectrum, and thus, the peak is assignable to C5 or C6 of **2** in Fig. 2a. Furthermore, the cross peak between H_j and the peak at 131.6 ppm, which is assignable to C5, was observed in the HMBC spectrum. Therefore, the peak at 150.4 ppm is assigned to C6 of **2**. In conclusion, the structure of **1-*p*-TolPyl-OMe** is determined to be **2**.

Table S1. Experimental and calculated excitation energies to the lowest excited state for **1-*p*-TolPyl-OMe**

Excitation Energy / eV		Oscillator Strength (Theor.)	Assignment (CI Coefficient)
Exptl.	Theor.		
3.22	2.8498	0.0213	93 -> 94 (0.68154)
3.55	3.7266	0.546	93 -> 95 (0.63745)

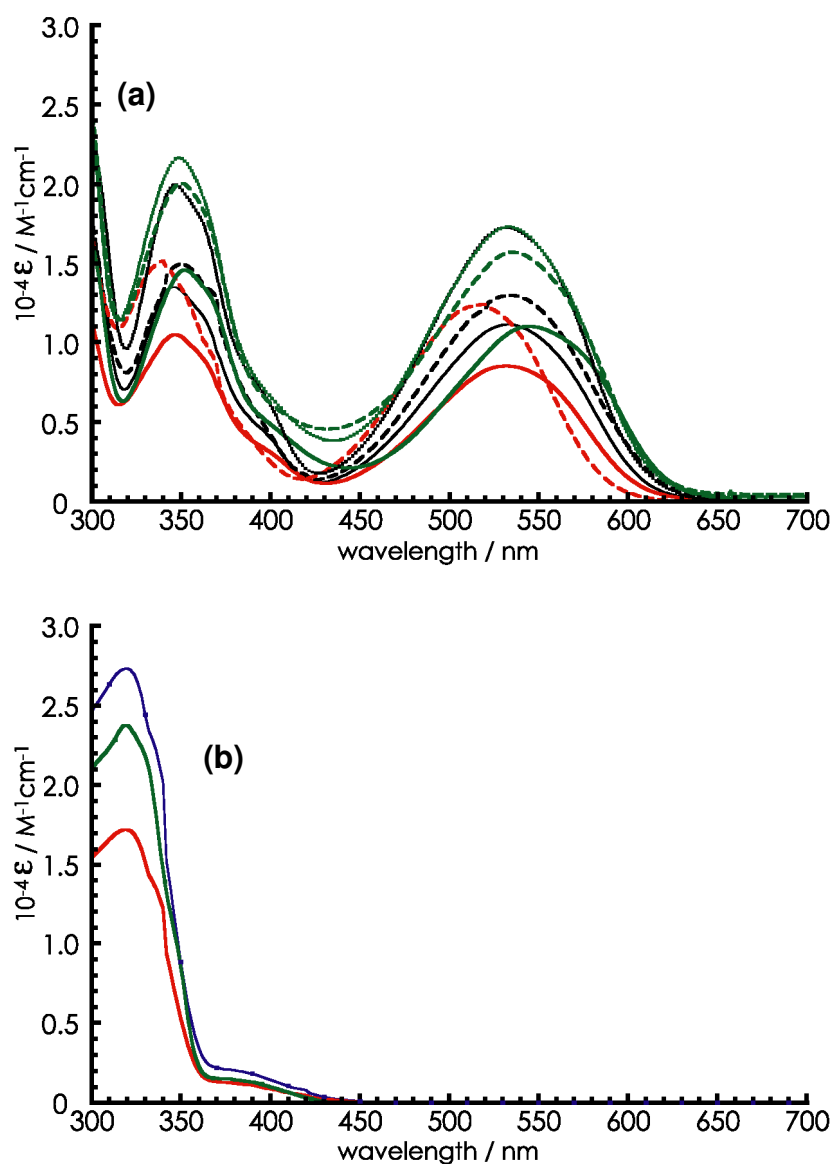


Figure S1. (a) UV-vis spectra of **1-p-TolPyl** in dichloromethane (black line), chloroform (black dashed line), 1,2-dichloroethane (black dotted line), benzonitrile (red line), acetonitrile (red dashed line), o-dichlorobenzene, (green line), toluene (green dashed line), and benzene (green dotted line). (b) UV-vis spectra of **1-p-TolPyl⁺** in methanol (red line), ethanol (blue line), and i-propyl alcohol (green line).

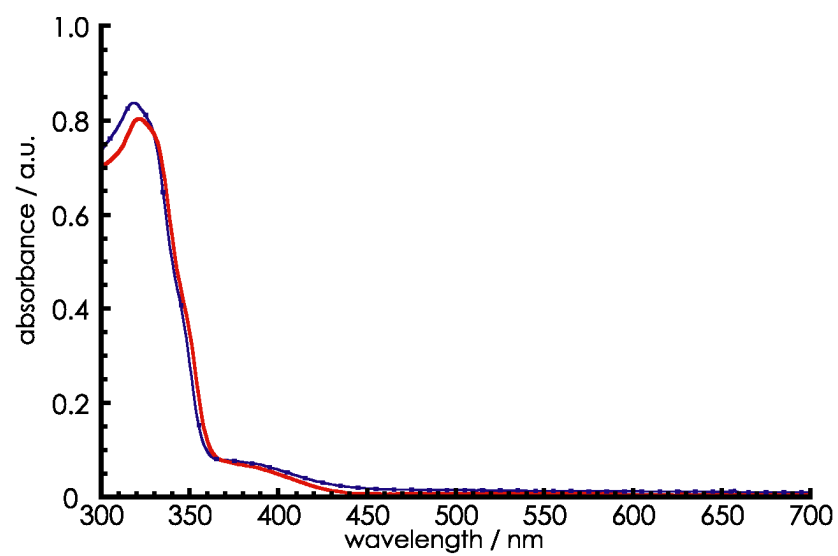


Figure S2. UV-vis spectra of **1-p-TolPyl** (blue line) in methanol and the isolated compound after reaction of **1-p-TolPyl** with NaOMe (red line) in dichloromethane.

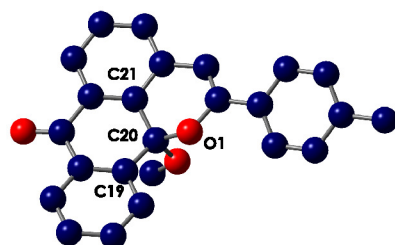


Figure S4. The optimized molecular structure of **1-*p*-TolPyl-OMe**.

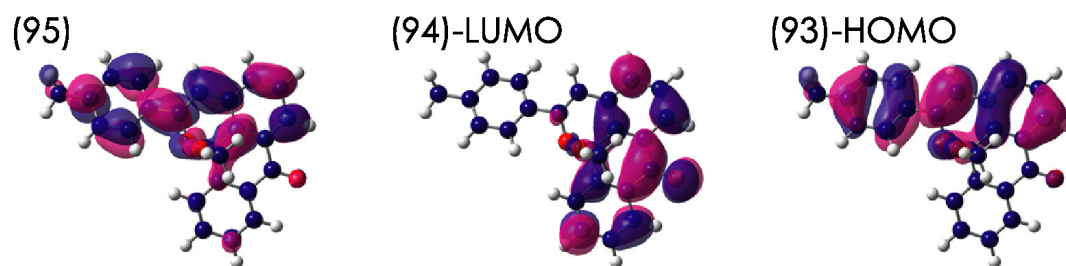


Figure S5. Molecular orbitals of **1-*p*-TolPyl-OMe** calculated at the B3LYP/6-31G +(p,d) level.

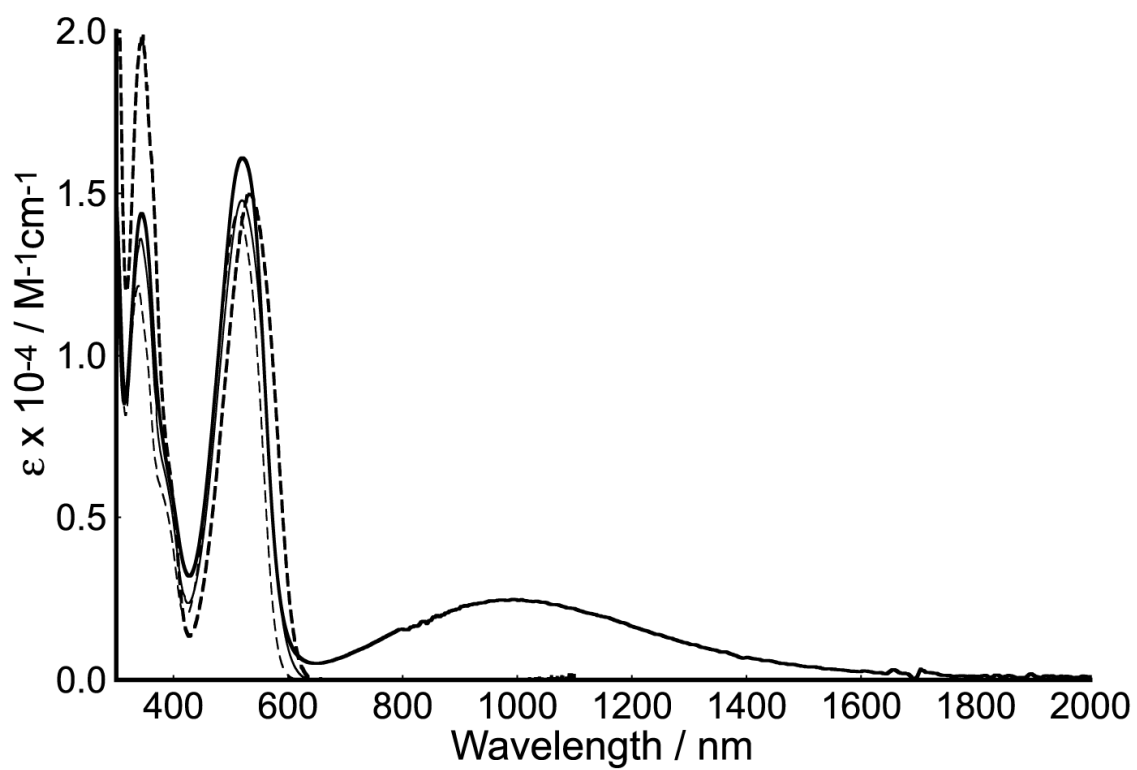


Figure S6. UV-vis-NIR spectra of **1-FcPyl⁺** (bold solid line), **1-p-TolPyl⁺** (bold dashed line), **1-m-TolPyl⁺** (solid line), **1-PhPyl⁺** (dashed line) in dichloromethane (0.5 mM).

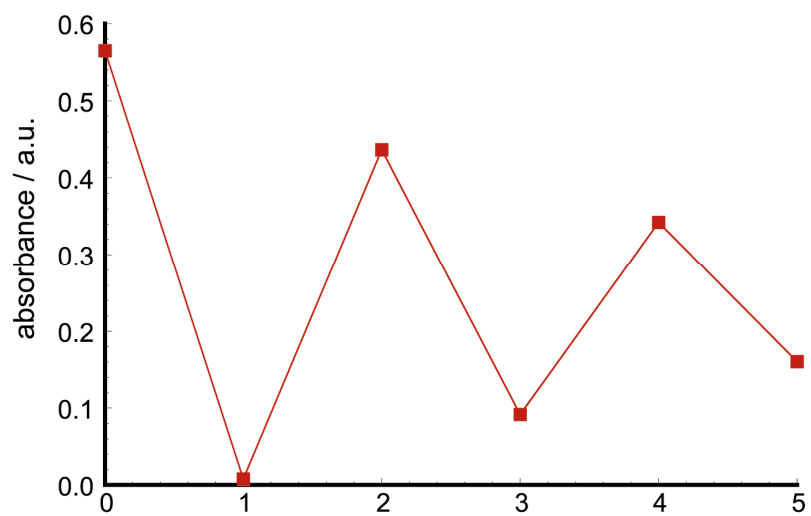


Figure S7. The changes of absorbance at 536 nm of **1-*p*-TolPyl⁺** upon the alternate addition of **TBACl** (1.0 eq.) and **TFSIH** (1.0 eq.) in 0.5 mM dichloromethane solution.