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'Lock and key' control of optical properties in a push-pull system

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We report the modulation of the absorbance of a flavin push–pull derivative through specific recognition by a complementary diamidopyridine (DAP), shifting the flavin intramolecular charge transfer band by ~30 nm.

Incorporating molecular recognition into donor–π-acceptor (D–π–A) molecules offers a potential strategy to create responsive push–pull materials for applications in optical data storage, telecommunications, nonlinear optics, and optical switching devices (including sensors). Push–pull materials combine electron donors (D) and acceptors (A) through a conjugated bond network to produce a D–π–A chemical motif with intrinsic properties: low-lying charge-transfer excited states, hyperpolarizability, solvatochromism, and second-order optical nonlinearities. Molecular recognition utilizes noncovalent interactions, such as hydrogen bonding, π-stacking, and electrostatics, to selectively assemble molecules into a particular orientation with its complementary counterparts. Coupling molecular recognition directly to push–pull materials provides an opportunity to build synthetic host–guest systems with tunable optical and electro-optical properties.

Current D–π–A systems do not utilize the advantages associated with molecular recognition, such as reversibility, specificity and directionality. Research has mainly focused on colorimetric responses of D–π–A systems in regards to subtle changes in pH or solvent polarity. For example, solvatochromic dyes such as Reichardt’s Dye and Methyl Red act as environmental indicators as they change color in different solvents primarily due to dipole–dipole and intramolecular solute–solvent interactions. The interactions remain relatively non-specific and function only as a response to the surrounding environment.

Our approach builds upon previous push–pull azobenzene derivatives, such as 4-nitro-4’-(dimethylamino)azobenzene, that demonstrate short fluorescent lifetimes (pico- and femto-second) and large solvatochromic charge transfer bands around ~400 nm. Direct conjugation to a flavin ring system creates an azobenzene flavin D–π–A push–pull derivative ABFL that contains molecular recognition capabilities (specifically three-point hydrogen bonding to the imido moiety) (Fig. 1).

The influence of molecular recognition on the optical properties of ABFL was determined via UV-Vis spectroscopy. Toluene was used as a solvent to promote specific three-point hydrogen bonding between ABFL and complementary diamidopyridine (DAP). Aliquots of DAP (stock solution 1.5 mM) were titrated into a constant host solution of ABFL (15 μM) and the resulting spectra were measured at each addition (Fig. 2). The spectra were corrected after each interval to eliminate any overlapping absorbance from DAP.

ABFL initially displayed a strong absorption at \(\lambda_{\text{max}} \sim 552\) nm in the visible spectrum providing a vivid purple color commonly associated with azobenzene dye derivatives. The strong absorption was assigned to an intramolecular charge transfer (ICT) and not an intermolecular charge transfer since dilution studies exhibited a linear correlation with absorbance intensity (see ESI†). As compared to similar push–pull azobenzene derivatives, ABFL exhibited a moderate bathochromic shift in ICT primarily due to the extended conjugation of ABFL. The weaker π–π* transition originally at \(\lambda_{\text{max}} \sim 335\) nm was attributed to the combination of flavin and azobenzene π–π* transitions.

Upon addition of DAP, a significant shift in the ICT and a noticeable color change (purple to blue) was observed for ABFL. There was a ~30 nm bathochromic shift (from 552 to 584 nm) for the ICT band and a slight increase in absorbance intensity. Furthermore, the weaker π–π* transition at 335 nm decreased while the peak at 374 nm increased upon addition of DAP (Fig. 2(b)). The resulting isosbestic points at 324, 346 and 424 nm implied that continuous additions of DAP shifted the equilibrium from an unbound ABFL + DAP to a bound state and it changed to the bound state ABFL–DAP.

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization, Kamlet-Taft parameters, and additional UV-Vis spectroscopy. See DOI: 10.1039/b718015b

Fig. 1 Representative ABFL D–π–A chemical structure and its molecular recognition capability via three-point hydrogen bonding.
[ABFL:DAP] state. The binding constant ($K_b$) for [ABFL:DAP] complex was calculated to be $K_b = \approx 1100 \text{ M}^{-1}$ (see ESI†) which was significantly larger than previous reported flavin host–guest complexes.17

A control MABFL (ABFL methylated at the N(3) position) was used to probe the specific molecular recognition binding process between ABFL and DAP. MABFL displayed similar electronic behavior (ICT $\approx 552$ nm) but remained relatively unaffected after addition of DAP. The methyl group at the N(3) position served to disrupt the three-point hydrogen bonding between MABFL and DAP. Additionally, methylation of DAP (see ESI†) provided a non-complementary hydrogen-bonding derivative which was used to further confirm the specific three-point hydrogen bonding process. Both the ICT and $\pi-\pi^*$ transitions remained unaltered upon addition of methylated DAP to ABFL indicating that the shift in absorbance was a direct result of the specific [ABFL:DAP] molecular recognition event.

The reversibility of the three-point hydrogen bonding between ABFL and DAP was examined via variable-temperature UV-Vis spectroscopy. The resultant endpoints from the titrations performed in toluene (15 $\mu$M ABFL with excess DAP) were used to evaluate the temperature dependence upon complex binding for both ABFL and MABFL (Fig. 3).

ABFL exhibited a $\approx 30$ nm blue shift in the ICT and an apparent color change (blue to purple) at $65^\circ$C. A re-emergence of pseudo-isosbestic points18 at $\approx 350$ and $\approx 410$ nm suggested that heating the solution reduced the hydrogen bonding for [ABFL:DAP] complex and shifted the dynamic equilibrium towards the unbound ABFL + DAP state. Control MABFL demonstrated a slight blue shift in ICT ($\approx 8$ nm) but did not exhibit any pseudo-isosbestic points or distinct color change in the presence of DAP. The results were consistent with a molecular recognition three-point hydrogen-bonding motif for [ABFL:DAP] complex.

In addition to the specific molecular recognition event for ABFL, both flavin molecules ABFL and MABFL were likewise solvatochromic. A comprehensive analysis of this solvatochromic effect of ABFL was performed to evaluate the nature of the ABFL “push–pull” character. ABFL was comprised of a neutral resonance form (I) that resembled a bond-alternate polyene structure19 and a zwitterionic resonance form (II) that exhibited a large charge separation on the order of $\approx 15$ Å (Scheme 1). The combination of these resonance contributions provided a strong “push–pull” electronic character for ABFL.

UV-Vis spectra of ABFL were recorded in eleven solvents with various polarities. Extra care was taken to compare all solvent samples at a constant ABFL concentration. Both ICT and $\pi-\pi^*$ transitions demonstrated a strong solvent dependence but did not exhibit a linear correlation to solvent polarity (see ESI†). Less polar solvents displayed a peak around $\lambda_{\text{max}} \approx 335$ nm and a prominent ICT at $\lambda_{\text{max}} \approx 544–556$ nm. Halogenated solvents, as well as more polar solvents, demonstrated various bathochromic shifts in ICT and $\pi-\pi^*$ transitions, suggesting that an additional solute–solvent interaction acted as a mechanism to stabilize ABFL.

Kamlet–Taft parameters20 in combination with linear free energy relationships (LFER) have been previously used to model solute–solvent interactions by describing solvents in terms of hydrogen bond donation ($\alpha$), hydrogen bond acceptance ($\beta$), and polarizability ($\pi^*$). We applied this strategy to reveal the extent of solute/solvent interaction for ABFL using specific Kamlet–Taft parameters from a similar electronic system (see ESI†).21 The contribution from each parameter ($\alpha$, $\beta$, $\pi^*$) to influence the resultant ICT absorption value was calculated as a coefficient in eqn (1).

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** Representative resonance structures of ABFL push–pull system: neutral (I) and zwitterionic (II) resonance forms.
of color of the solution from purple to blue and establishing our control over the noncovalent interactions. This process is reversible at elevated temperatures demonstrating negatively charged oxygen in the zwitterionic resonance form as a result of minimal pseudo-isosbestic points obtained as a result of minimal solvatochromism. 

In conclusion, we have the ability to tune the electrons and hence color of the ABFL “push–pull” system via molecular recognition. The addition of complementary DAP shifts both ICT and π–π* transitions (~30 nm) in toluene, changing the color of the solution from purple to blue and establishing an equilibrium between bound and unbound states. Stabilization of ABFL via hydrogen bonding occurs specifically at the negatively charged oxygen in the zwitterionic resonance form as indicated by its solvatochromic response. The binding process is reversible at elevated temperatures demonstrating our control over the noncovalent interactions.

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Notes and references


12. A large excess of DAP was necessary to promote an observable color change at such a dilute concentration of ABFL.


16. There was no apparent trans–cis isomerization as both 1H NMR and UV–Vis spectra demonstrated no changes after continuous irradiation at 365 nm. However, further investigation may be needed to confidently eliminate any rotation around the N–N bond as seen in the following references: (a) S. A. Nagamani, Y. Norikane and N. Tamaoki, J. Org. Chem., 2005, 70, 9304; (b) H. Kang, A. Facchetti, H. Jiang, E. Cariati, S. Righetto, R. Ugo, C. Khmelinskii, J. Komasa, M. Insinska-Rak and M. Sikorski, THEOCHEM, 2005, 756, 47; (c) M. D. Greaves, R. Deans, T. H. Galow and V. M. Rotello, Chem. Commun., 1999, 785.


18. Only pseudo-isosbestic points were obtained as a result of minimal solvent loss which lead to a slight increase in absorbance intensity for both ABFL and MABFL as a function of temperature.

