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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) [1] molecules offers a potential strategy to create responsive push–pull materials for applications in optical data storage,[2] telecommunications,[3] nonlinear optics,[4] and optical switching devices (including sensors).[5] 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.[6] 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.[7] For example, solvatochromic dyes such as Reichardt's Dye[8] and Methyl Red[9] act as environmental indicators as they change color in different solvents primarily due to dipole–dipole and intermolecular 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.[10] Direct conjugation to a flavin ring system creates an azobenzene flavin D–π–A push–pull derivative 8-[[*p*-[bis(ethyl)amino]phenyl]azo]isobutylflavin (**ABFL**) that contains molecular recognition capabilities (specifically three-point hydrogen bonding to the imido moiety) (Fig. 1).[11]

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)[12] 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 $\lambda_{\max}$ ∼552 nm in the visible spectrum providing a vivid purple color commonly associated with azobenzene dye derivatives.[13] The strong absorption was assigned to an *intra*molecular charge transfer (ICT) and not an *inter*molecular 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 $\lambda_{\max}$ ∼335 nm was attributed to the combination of flavin[14] and azobenzene[15] 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

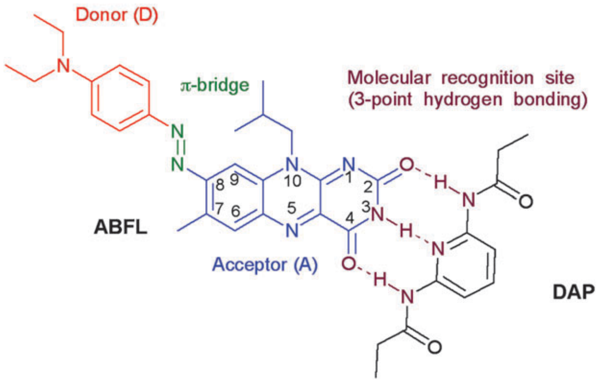

Fig. 1 Representative **ABFL** D–π–A chemical structure and its molecular recognition capability *via* three-point hydrogen bonding.

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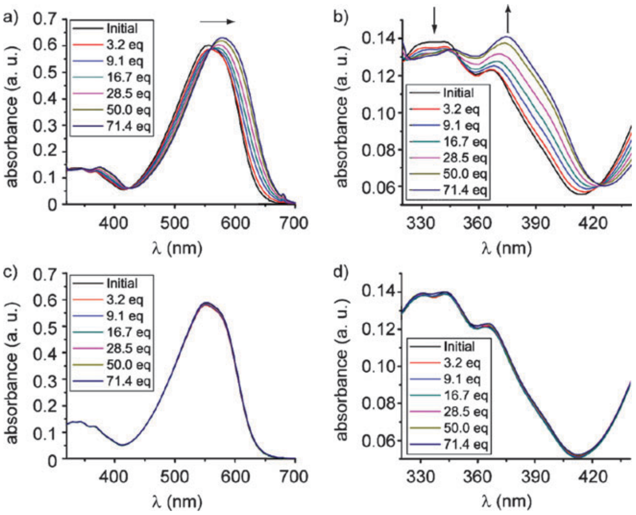


Fig. 2 UV-Vis titrations of **DAP** into **ABFL** (a, b) and **MABFL** (c, d) performed at 25 °C in toluene. Curves show entire spectrum (a and c) and expanded regions in the range 320–430 nm (b and d).

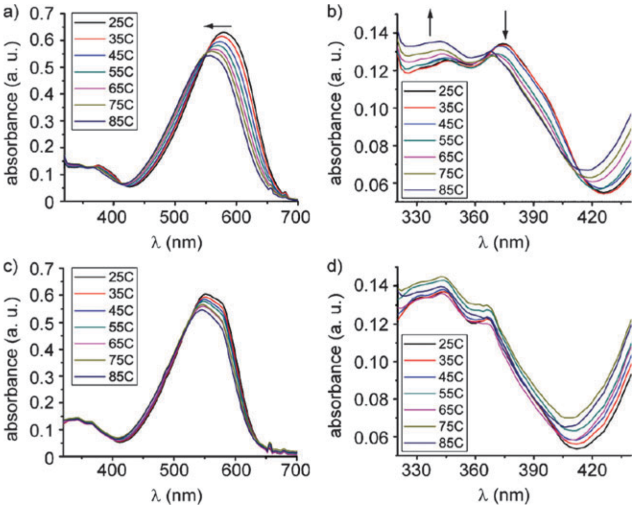


Fig. 3 Variable temperature UV-Vis for **ABFL** (a, b) and **MABFL** (c, d) in toluene. Curves show entire spectrum (a) and (c) and expanded regions in the range 320–430 nm (b) and (d).

[ABFL:DAP] state.[16] The binding constant (K_a) for **[ABFL:DAP]** complex was calculated to be $K_a = \sim 1100\ M^{-1}$ (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 ~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 π–π* 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.

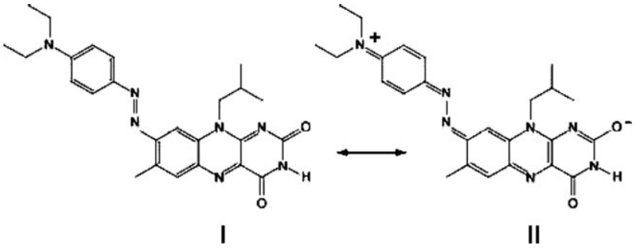
The reversibility of the three-point hydrogen bonding between **ABFL** and **DAP** was examined *via* variable-temperature UV-Vis spectroscopy. The resultant endpoints from the titrations performed in toluene (15 μM **ABFL** with excess **DAP**) were used to evaluate the temperature dependence upon complex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

ABFL exhibited a ~30 nm blue shift in the ICT and an apparent color change (blue to purple) at 65 °C. A re-emergence of psuedo-isosbestic points[18] at ~350 and ~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 (~8 nm) but did not exhibit any psuedo-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 structure[19] and a zwitterionic resonance form (**II**) that exhibited a large charge separation on the order of ~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 π–π* 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 λ_{max} ~335 nm and a prominent ICT at λ_{max} ~544–556 nm. Halogenated solvents, as well as more polar solvents, demonstrated various bathochromic shifts in ICT and π–π* transitions, suggesting that an additional solute–solvent interaction acted as a mechanism to stabilize **ABFL**.

Kamlet–Taft parameters[20] 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 (α), hydrogen bond acceptance (*β*), and polarizability (*π**). 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 (α, *β*, *π**) to influence the resultant ICT absorption value was calculated as a coefficient in eqn (1).



Scheme 1 Representative resonance structures of **ABFL** push–pull system: neutral (**I**) and zwitterionic (**II**) resonance forms.

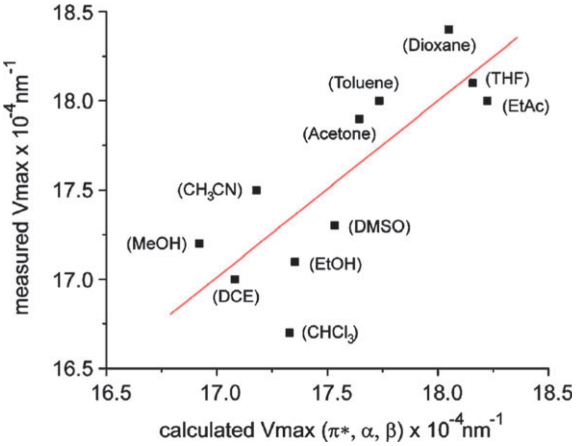


Fig. 4 Analysis of **ABFL** using Kamlet–Taft parameters exhibiting strong dependence on polarity and hydrogen bond donating solvents.

$$V_{\max} = 18.824 - 2.318\pi^* - 1.433\alpha - 1.351\beta \qquad (1)$$

The $V_{\max}$ values for the predicted ICT absorption were expressed in kilokaysers (1 kK = 10^{-4} nm^{-1}) for comparison with previous solute probes using Kamlet–Taft parameters. Calculated $V_{\max}$ values were plotted against the measured $V_{\max}$ obtaining a relatively linear correlation. All three parameters (α, β, π^*) had a significant impact on the ICT of **ABFL** as observed from the LFER analysis (Fig. 4). Both polar and hydrogen-bond donating solvents appeared to stabilize an **ABFL** excited state consistent with a more zwitterionic form. As a result, the ICT shifted to a longer wavelength for polar and hydrogen-bond donating solvents. Less polar solvents and hydrogen-bond accepting solvents destabilized **ABFL** shifting the ICT to a shorter wavelength. Control **MABFL** exhibited similar push–pull behavior in the UV-Vis spectra with respect to the various solvents (see ESI†). This result indicated that the effective hydrogen bonding between hydrogen-bond donating solvents and the negatively charged oxygen in the zwitterionic form was the main contribution to the stabilization of the flavin push–pull system.

In conclusion, we have the ability to tune the electronics 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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