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1. Introduction

Tautomers are readily interconverted constitutional isomers, usually distinguished by a rearrangement of a labile hydrogen atom and a double bond (*e.g.*, enol–keto tautomerization).¹ The equilibrium between tautomers is often rapid under normal conditions, being catalyzed by traces of acid or base present in most samples and solvents.² Proton tautomerization is central to several fields of chemistry and biochemistry and plays a role in pharmaceutical activity, enzyme activity, stabilization of base pairs in duplex DNA, and self-assembly.^{3,4} *ortho*-Hydroxy aromatic azomethines (known as Schiff bases) possessing intramolecular

Experimental and theoretical study of enol-keto prototropic tautomerism and photophysics of azomethine-BODIPY dyads[†]

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In this study we report about two novel azomethine-BODIPY dyads 1 and 2. The two dyads have been, respectively, synthesized by covalent tethering of tautomeric ortho-hydroxy aromatic azomethine moieties including N-salicylideneaniline (SA) and N-naphthlideneaniline (NA) to a BODIPY fluorophore. Both of the two dyads 1 and 2 show enol-imine (OH) structures dominating in the crystalline state. Dyad 1 in the enol state is the most stable form at room temperature in most media, while enol-keto prototropic tautomerism of the NA moiety in solution is preserved in dyad 2, which can be reversibly converted between enol and keto forms in the environment's polarity. Visible illumination of dyad 2 in the enol state excites selectively the BODIPY fragment and then deactivates radiatively by emitting green light in the form of fluorescence, while the emission intensity of 2 in the keto state is guenched on the basis of the proton-coupled photoinduced electron transfer (PCPET) mechanism. This allows large fluorescence modulation between the two states of dyad 2 and generates a novel tautomerisable fluorescent switch. Theoretical calculations including calculated energies, potential energy surfaces (PESs) and intrinsic reaction coordinate (IRC) analysis further support that the single proton transfer reaction from an enol form to a transition state (TS) and from the TS to a keto form for 2 is easier to occur than that for 1, which accounts for the fluorescence quenching of 2 in methanol. The agreement of the experimental results and theoretical calculations clearly suggests that fluorescent and tautomeric components can be paired within the same molecular skeleton and the proton tautomerization of the latter can be designed to regulate the emission of the former. In addition, preliminary experiments revealed that 1 can be potentially used as a simple on/off fluorescent chemosensor which exhibited higher selectivity for Cu²⁺ over other common cations.

> hydrogen-bonding are an interesting class of compounds for theoretical and experimental studies because they can undergo proton-tautomerism reaction leading to interesting properties including thermo- and photochromism. As proton transfer in these systems causes a change in optical properties, these molecules can be utilized for the design of various optical switches and storage devices.5 Due to significances of proton transfer and tautomerism processes, there have been numerous studies of the ortho-hydroxy aromatic azomethines in the solid-state and in solution. Generally, they display two possible tautomeric forms, the enol-imine (OH) form and the keto-enamine (NH) form. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in the ortho-hydroxy aromatic Schiff bases: O-H···N in enol-imine and N-H···O in keto-enamine tautomers. The enol-imine form is the most stable form at room temperature but is in equilibrium with the keto-enamine form relying on the substitution patterns of the aromatic rings and the surrounding medium.⁶ Different analytical methods have been used to show the presence of the enol-imine and ketoenamine forms, among them are UV-vis, fluorescence, Raman,



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FT-IR, and NMR spectroscopy and X-ray crystallography techniques, as well as combinations thereof.⁷ As a complement to these experiments, a variety of computational chemistry methods has also been applied.⁸ Both experimental and theoretical investigations have shown that the reversible enol–keto tautomerism occurs *via* an intramolecular H-transfer mechanism between *ortho*-hydroxy and imine nitrogen forms.⁸ Enol–keto tautomerism has been used to modulate magnetic dynamics of some lanthanide complexes.⁹ However, relatively less attention has been paid to attachment of *ortho*-hydroxy azomethine fragments to organic chromophores to study the effect of the enol \leftrightarrow keto tautomerism reaction on photophysical properties of chromophores.

Seeking to look for suitable organic chromophores in favor of grafting tautomeric components, our attention has turned to the boron dipyrromethene (4,4-difluoro-4-bora-3a,4a-diaza-sindacene, BDP or BODIPY) class of dyes. Recent efforts by other groups and our laboratory have focused on developing BODIPY fluorescence sensors based on photoinduced electron transfer (PET) as a transduction mechanism.¹⁰ BODIPYs are well-known for their excellent photophysics such as strong absorption of visible light, high fluorescence quantum yields and good photostability.^{10,11} In addition, the optical properties of BODIPY are tunable through structural modifications on the core of dye. These favorable features render BODIPY as widely used as a fluorophore core for the construction of luminophores, molecular probes or molecular logic gates, light-harvesting molecular arrays and photodynamic therapy (PDT) agents.¹¹ In this context, we decided to explore the possibility of integrating fluorescent and tautomeric components within the same molecular skeleton. We report herein the synthesis, structures, photophysical properties of two dyads (1 and 2) with high thermal stabilities, which consist of ortho-hydroxy aromatic azomethines including N-salicylideneaniline (SA) and N-naphthlideneaniline (NA) coupled to a BODIPY fluorophore. Significant differences in the photophysical behaviours of the two synthesized dyads related to protontautomerism are observed and discussed with the aid of density functional theory (DFT) calculations.

2. Results and discussion

2.1. Synthesis and characterization

The starting BODIPY-linked aniline **3** was firstly synthesized in moderate yield from a reaction of 2,4-dimethylpyrrole and 4-nitro-benzaldehyde, followed by a conversion of the -NO₂ group to form an -NH₂ substitute according to reported procedures.^{10e,12} With the main aim of investigating the effect of prototropic tautomerism of *ortho*-hydroxy aromatic Schiff bases on the photophysics of BODIPY chromophores, azomethine-BODIPY dyads **1** and **2** functionalized with imines were prepared by a convenient one-step condensation reaction of **3** with 2-hydroxybenzaldehyde or 2-hydroxynaphthaldehyde in a high yield according to the synthetic procedures along with individual Schiff bases (**SA** and **NA**) as well as a model **TM-BODIPY**, as shown in Scheme 1. Dyads **1** and **2** were first documented by single-crystal X-ray crystallography (SCXRD) and further



Scheme 1 Design and synthesis of dyads 1 and 2.

characterized by standard analytical techniques (i.e., FT-IR spectroscopy, NMR spectroscopy, mass spectrometry, elemental analysis and cyclic voltammetry), which gave satisfactory data corresponding to their molecular structures. Solid-state IR spectra of 1 and 2 were recorded in the 4000–400 cm^{-1} region (Fig. S1 of ESI⁺). Generally, the non-hydrogen-bonded or a free hydroxyl group absorbs strongly in the 3550–3700 cm⁻¹ region.¹³ Intramolecular hydrogen bonding if present in the six-membered ring system would reduce the O-H stretching band to the 3550–3200 cm⁻¹ region.¹⁴ IR spectra of 1 and 2 show a sharp band at 3441 and 3442 cm^{-1} due to O–H stretching vibration. The characteristic region of 1700–1500 cm⁻¹ can be used to identify the proton transfer of Schiff bases. Azomethine (C=N) bond stretching vibration was observed at 1623 and 1626 cm^{-1} for 1 and 2. The crystal phase purities of 1 and 2 were confirmed from powder X-ray diffraction (PXRD) patterns (Fig. S2 of ESI[†]). The thermal behavior of 1 and 2 as well as of SA and NA was studied by differential scanning calorimetry (DSC) (Fig. S3 of ESI[†]). The DSC thermogram of 1 and 2 exhibited only one exothermic peak at 288 °C $(\Delta H = 107.9 \text{ J g}^{-1})$ and 299 °C ($\Delta H = 86.21 \text{ J g}^{-1}$), respectively, ascribed to the melting point (T_m) of dyads. Obviously, the two dyads exhibit a higher melting point and are more stable than starting material 3 ($T_{\rm m}$ = 190 °C) or reference Schiff bases SA $(T_{\rm m}$ = 52 ± 1 °C) and NA $(T_{\rm m}$ = 96 ± 1 °C).

The redox behaviour of the two dyads was investigated using the cyclic voltammetry (CV) technique in dry DCM containing a 0.1 M TBAP background electrolyte (Table S1 of ESI[†]). For these dyads, a single electrochemical peak is observed on reductive scans that could be ascribed to formation of the BODIPY π -radical anion (-1.69 V for 1 and -1.59 V for 2). On oxidative scans, two peaks corresponding to the oxidation of the Schiff base fragment and the formation of the BODIPY π -radical cation are observed for 1 and 2. For 2, there is a slight negative shift of the oxidation peak from the Schiff base fragment (0.62 V) compared with that of 1 (0.80 V) due to the redundant benzene ring. The oxidation potentials of the BODIPY moiety in these dyads are similar (1.01 V for 1 and 1.04 V for 2). From these results of electrochemistry, it is inferred that the Schiff base unit and the BODIPY group are isolated and only minor, if any, electronic communication takes place through the bridge in the ground state.

2.2. Crystal structural analyses

Crystalline samples of azomethine–BODIPY dyads 1 and 2 were obtained by a slow vapour diffusion of hexane into a saturated



Fig. 1 Single crystal X-ray diffraction structures of **1** (a), **2** (b) with thermal ellipsoids set at 50% probability, and the theoretical geometric structures of **1** (c) and **2** (d).

CHCl₃ solution of 1 or CH₂Cl₂ solution of 2. Single crystals collected were of suitable quality to undertake a structure determination by SCXRD analysis, and crystallographic data are given in Table S2 (ESI[†]). Both 1 and 2 crystallize in the triclinic space group $P\bar{1}$ with one independent molecule within the asymmetric unit (Fig. 1a and b). In fact, each azomethine-BODIPY dyad constitutes a BODIPY unit as the fluorophore and a Schiff base fragment as a tautomer. As previously observed in some similar structures, 10d,15 the BODIPY core B(N₂F₂) shows a quasi-tetrahedron configuration with the average angle of F-B-F of 108.8° and the average bond length of B–N and B–F to be 1.544 Å and 1.388 Å, respectively (Table S3 in the ESI[†]). In the BODIPY moiety, the C₉BN₂ framework consisting of one central six-membered and two adjacent five-membered rings is essentially flat, with the maximum deviation from the least-squares mean plane for the 12 atoms of the indacene group being 0.083 Å in 1 and 0.029 Å in 2, respectively. This geometry indicates the strongly delocalized π -system nature of the C₉BN₂ framework in 1 and 2. However, this π -electron delocalization is interrupted between the two B-N bonds (1.536-1.554 Å), which is in agreement with the results reported for other BODIPYs.15 It was revealed that the introduction of two methyl groups at C-1 and C-7 positions in the BODIPY core in 1 and 2 prevents the free rotation of the meso-phenyl moiety, resulting in an almost orthogonal configuration between the BODIPY core and the mesobenzene moiety. The dihedral angle between the meso-phenyl ring and the indacene plane (87.6°) in 1 is analogous to that in 2 (86.5°) , indicating the almost nonelectronic coupling nature between the meso-phenyl ring and the C_9BN_2 unit in 1 and 2.

From the ORTEP view, the dihedral angle between the aromatic ring systems in the Schiff base moiety of **1** is 26.1°. This dihedral angle decreases to 4.1° in **2**. In general, *ortho*-hydroxy Schiff bases undergo tautomerism involving proton transfer from the hydroxylic oxygen to the imino nitrogen atom. The process of proton transfer ends up with two tautomeric forms known as enol and keto structures. The C7–N1 and C5–O1 bonds for **1** as well as C11–N1 and C7–O1 bonds for **2** are the most important indicators of the tautomeric types. The C5–O1 and C7–O1 bonds are double bonds for the keto-enamine tautomers, whereas these bonds display single bond character in the enol-imine tautomers. The C7–N1 and C11–N1 bonds are also double bonds in the enol-imine tautomers and of single bond length in the keto-enamine tautomers. SCXRD reveals the preference of the enol structure in the Schiff base moiety in the solid state for 1 and 2, as indicated by the bond parameters (C5–O1 = 1.359 Å, C7–O1 = 1.329 Å and C7–N1 = 1.285 Å, C11–N1 = 1.291 Å). Furthermore, the aromaticities of enol forms of 1 and 2 can also be inferred from the harmonic oscillator model aromaticity (HOMA) index.¹⁶ The HOMA indices in the range of 0.900-0.990 and 0.500-0.800 correspond to aromatic and the non-aromatic rings, respectively. In 1, the calculated HOMA indices for C1/C6 and C8/C13 are 0.968 and 0.992, respectively. These results show that C1/C6 and C8/C13 in 1 have purely aromatic character. In 2, the calculated HOMA indices for C5/C10 and C12/C17 are 0.629 and 0.995, respectively, which display that C12/C17 has purely aromatic character while C5/C10 deviated from aromaticity. This difference in molecular configuration is responsible for different results of theoretical calculations and optical properties as discussed below.

The existence of strong intramolecular O1-H1D...N1 and O1–H1B···N1 hydrogen bonds both producing S(6) ring motifs is observed in 1 and 2, respectively. These H-bonds can be characterized by O1···N1 distances and are summarized in Table 1. It is known that there is a strong correlation between the strength of the H-bond and the delocalization of the system of conjugated double bonds, and the effect is qualitatively interpreted by the resonance-assisted hydrogen bond (RHAB) model.¹⁷ The observed O···N distances of 2.605(4) Å for 1 and 2.548(2) Å for 2 are apparently shorter than 2.656 Å which was reported for O-H···N in the class of the RAHB model. The aggregations of 1 and 2 through a series of weak hydrogen bonds including C–H···F and edge-face C–H··· π interactions in the crystal cells are shown in Fig. S4 in the ESI.† These F- and C-based interactions can be further visualized by Hirshfeld surface calculations and given in Fig. S5 in the ESI.†

2.3. Computational studies

The optimized parameters (bond lengths, bond angles, and dihedral angles) of dyads **1** and **2** have been obtained using the *Gaussian 09* program with density functional theory (DFT), the B3LYP method, and 6-31+G(d,p) as the basis set. The optimized structures of **1** and **2** are depicted in Fig. 1c and d with numbering of the atoms. The calculated structural parameters of **1** and **2** are presented in Table S3 (ESI[†]) along with the corresponding values obtained from the experimental data. When the X-ray structures of **1** and **2** are compared to their optimized counterparts, the bond lengths and bond angles computed by the B3LYP method show a good correlation with the experimental values. The remarkable conformational discrepancies are observed in the orientation of the *meso*-phenyl ring in **1** and **2**. The orientation

Table 1 Experimental and theoretical hydrogen-bond geometries (Å, deg) for ${\bf 1}$ and ${\bf 2}$

D−H···A	D-H	$H{\cdots}A$	$D{\cdots} A$	D−H· · ·A
X-ray diffraction for 1	1.02(4)	$1.65(5) \\ 1.74 \\ 1.61(3) \\ 1.65$	2.605(4)	153.8(3)
B3LYP/6-31+G(d,p) for 1	1.00		2.634	147.2
X-ray diffraction for 2	1.02(2)		2.548(2)	150.9(2)
B3LYP/6-31+G(d,p) for 2	1.01		2.563	148.0

of the meso-phenyl ring is defined by the torsion angles C7-N1-C8-C13 [153.1(2)° for 1] and C11-N1-C12-C17 [177.2(1)° for 2]. These torsion angles have been calculated to be 145.06° and 146.11° for B3LYP, respectively. Such conformational discrepancies can be explained by the fact that the calculations assume an isolated molecule where the intermolecular Coulombic interaction with the neighboring molecules is absent, whereas the experimental results correspond to interacting molecules in the crystal lattice, as described in the aforementioned crystal structure analysis. When the geometries of hydrogen bonds in the optimized structures of 1 and 2 are examined, it is seen that O-H...N intramolecular hydrogen bonds exist between the phenol O atom for 1 (naphthol O atom for 2) and the imine N atom. For 1, O–H, H···N, and O–H···N values are 1.02(4) Å, 1.65(5) Å, and 153.8(3)° for X-ray diffraction, and 1.00 Å, 1.74 Å, and 147.2° for B3LYP. For 2, O-H, H...N, and O-H...N values are 1.02(2) Å, 1.61(3) Å, and 150.9(2)° for experimental data, and 1.01 Å, 1.65 Å, and 148.0° for theoretical values. There is good matching between the calculated hydrogen-bond geometries and those obtained from the X-ray diffraction structures. The presence of the hydrogen bond appears to be an important property of the molecule, stabilizing its conformation in the crystal, as shown in the molecular modelling part, this is also visible in the model obtained for the molecules discussed.

The enol-imine (NH) and keto-enamine (OH) tautomerisms of dyads 1 and 2 are given in Scheme S1 (ESI⁺). To investigate these tautomeric stabilities, quantum chemical calculations were carried out for the enol and keto forms of 1 and 2. Some important physicochemical properties such as total, HOMO, and LUMO energies and the dipole moment (μ) were also calculated with the same level of theory, and the results are given in Table 2. First comparing the total energies of the two tautomers for 1, the enol tautomer is substantially more stable (4.91 kcal mol^{-1}) than the keto form. This is an expected result since the enol form of 1 has two purely aromatic rings as supported by the above structural analysis and ortho-hydroxy azomethine generally prefers the enol structure. The intramolecular proton transfer for 1 was investigated in the gas phase by performing a potential energy surface (PES) scan at the B3LYP/6-31+G(d,p) level in order to determine its effects on the molecular geometry. The process was started from optimized enol-imine geometry by selecting the O-H bond as a redundant internal coordinate. The graph of the relative energy versus the O-H bond distances is given in Fig. 2. The energy values were calculated relative to the energy of the

Table 2Calculated energies, dipole moments, and frontier orbital energiesin vacuum and in methanol for 1 and 2 and their tautomers

	Tautomer	E_{TOTAL} (hartree)	$E_{\mathrm{HOMO}}\left(\mathrm{eV}\right)$	E_{LUMO} (eV)	μ (D)
Gas phase $(\varepsilon = 1)$	1-enol 1-keto 2-enol 2-keto	$\begin{array}{r} -1469.54123405\\ -1469.53340411\\ -1623.18996163\\ -1623.18870347\end{array}$	-5.6793 -5.7579 -5.6602 -5.7209	-2.7007 -2.7884 -2.6814 -2.7483	4.8157 3.8781 5.4163 4.4635
CH ₃ OH (ε = 32.7)	1-enol 1-keto 2-enol 2-keto	$\begin{array}{r} -1469.55686104\\ -1469.55389163\\ -1623.20631485\\ -1623.20871348\end{array}$	-5.8172 -5.8317 -5.8143 -5.8153	-2.8177 -2.8398 -2.8145 -2.8313	6.7180 5.5145 7.2598 5.9880



Fig. 2 Relative energy profiles during the proton transfer process of **1** (a) and **2** (b).

stable enol form. Fig. 2a shows two minima representing the stable forms of **1**. The keto form corresponds to a local minimum while the global minimum represents the stable enol form. The potential energy barrier needed for the enol to keto form conversion process in **1** was calculated to be 6.08 kcal mol⁻¹.

We have also considered 2 for further study to know whether the nature of proton transfer of 1 and 2 is the same. As seen from Table 2, the calculated total energy of the enol form of 2 is only slightly lower than the keto form in the gas phase (0.81 kcal mol⁻¹). Similar to dyad 1, PES scan of 2 shows two distinct minima corresponding to enol and keto tautomers. Here the enol form is slightly stable than the keto form. The energy barrier in going from the enol to keto form is 3.34 kcal mol⁻¹, which is obviously smaller than that of 1. Such a small energy barrier is easily overcome by a light-weight particle, such as a proton at room temperature. Therefore, at the ground state there will always be a mixture of keto and enol forms with a larger percentage of the enol form in the gas phase and the keto form in solution.

To further examine the whole process of enol-keto tautomerization via single proton transfer in dyads 1 and 2 in more detail, we performed an intrinsic reaction coordinate (IRC) analysis for each case (see ESI[†]). The nature of the stationary points was confirmed by means of a vibrational analysis. The whole prototropic tautomerism process of 1 and 2 is actually subdivided into two parts: (i) transfer from the enol form (OH) to the transition state (TS) and (ii) from the TS to the proton transfer keto form (NH). Fig. 3 shows the calculated free energy profiles and the structures of the enol form, TS, and keto form for 1 and 2. For enol-keto tautomerization of 1, the free energy of the keto form is very close to that of the TS $(3.4 \text{ kcal mol}^{-1} \text{ vs. } 3.5 \text{ kcal mol}^{-1})$ while larger than that of the enol form (3.4 kcal mol^{-1} vs. 0 kcal mol^{-1}). While for 2, both the barrier energy and product free energy are on the verge of the reactant free energy (1.4 kcal mol⁻¹ vs. 0.8 kcal mol⁻¹ vs. 0 kcal mol⁻¹). These calculated results indicate that compared to 1, the single proton transfer reaction of 2 is easier to occur, and 2 is more inclined to obtain an enol-keto mixture while 1 is not. With a closer analysis of structures, we can see that both the structures of reactants and transition states of 1 and 2 exist differently while the product states are similar. For the reactant state, the distance of the N-H hydrogen-bond of the reaction center in 1 is larger than that in 2, indicating that the proton transfers from the O atom to the N atom are more relaxed in 2. For the TS, the distances of N-H and O-H are equivalent in 2 while in 1 the distance of O-H is larger than that of N-H, indicating that the structure of the TS is similar to the structure



Fig. 3 Transition state from enol to keto form of 1 (a) and 2 (b) at the B3LYP/6-31+G(d,p) level (kcal mol^{-1}).

of the product state in **1** and to some extent means that the proton-transfer-distance from the reactant to the TS in **1** is longer than that in **2**. Therefore, the single proton transfer reaction of **2** is easier to occur. The reason for this result may be the redundant benzene ring of **2** which could increase the conjugative effect and the resonant structure compared to **1** (Fig. S6 in the ESI[†]).

2.4. Photophysical properties

The optical properties of **1** and **2** were first characterized by using UV-vis absorption spectroscopy in solvents of varying polarity (Table 3 and Fig. S7 of ESI[†]). Fig. 4 shows the absorption spectra of **1** and **2** as well as of references **SA** and **NA** in CH₃OH. The absorption spectra of the studied dyads exhibit features that can be easily assigned to specific subunits. **SA** exhibits two moderate absorption peaks centered at 269 nm and 348 nm, respectively, assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.¹⁸ The model **TM-BODIPY** presents a sharp and intense absorption peak at 500 nm (Fig. S8 in the ESI[†]),¹⁹ a typical feature of the BODIPY dyes.¹⁵ The absorption spectrum of dyad **1** is nearly the superposition of the spectra of **SA**

Table 3 Spectral parameters of 1 and 2 in different solvents

	Solvent	$E_{\mathrm{T}}(30)^a$ (kcal mol ⁻¹)	λ _{abs} (max/nm)	$\log_{(\epsilon_{\max})}$	λ _{em} (max/nm)	${\Phi_{\mathrm{fl}}}^b$
1	MeOH	55.4	499	4.92	512	0.38
	CH ₃ CN	45.6	498	4.93	511	0.48
	THF	37.4	501	4.95	515	0.53
	CH_2Cl_2	40.7	502	4.95	516	0.55
	Toluene	33.9	505	4.92	518	0.57
2	MeOH	55.4	499	4.93	513	0.05
	CH_3CN	45.6	498	4.94	512	0.03
	THF	37.4	501	4.95	516	0.30
	CH_2Cl_2	40.7	502	4.95	516	0.27
	Toluene	33.9	505	4.96	519	0.40

^{*a*} Solvent polarity index. ^{*b*} 1,3,5,7-Tetramethyl-8-phenyl–BODIPY was used as a standard ($\Phi_{\rm fl}$ = 0.72 in tetrahydrofuran).



Fig. 4 UV-Vis absorption spectra of 1 and SA (a) as well as of 2 and NA (b) in methanol at room temperature, path length 1.0 cm, concentration 1×10^{-5} M for each sample.

and **TM-BODIPY**. The absorption maximum (499 nm) of **1** with the molar absorption coefficient as high as $8.03 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ is as expected for the **TM-BODIPY** dye, which is due to the 0–0 vibrational band of the $S_0 \rightarrow S_1 (\pi - \pi^*)$ transition localized on the BODIPY unit.¹⁹

Dyad 2 also shows an intense absorption band centered at 499 nm with the absorption coefficient of around 7.97 imes $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. In addition, 2 displays a shoulder at the short wavelength (high-energy) side, centered at about 469 nm, and is attributed to the 0-1 vibrational band of the same transition. The moderate higher-energy transitions of the NA unit in 2 were observed at 315 and 375 nm, attributed to π - π * transition of the enol form of NA. Interestingly, an absorption band at 438 nm was observed in the spectrum of 2 in CH₃OH, which may belong to the keto form of ortho-hydroxy Schiff bases.²⁰ In contrast, any band belonging to the keto-enamine form in 1 was not observed with a value greater than 400 nm. Referring to previous studies it was concluded that 2 exists in both enol and keto forms in CH₃OH while 1 is in favor of the enol state and not in keto in most organic solvents at room temperature.^{8a,21} The keto form is important in the solution and stabilized by the polar solvents through solute-solvent interactions. Here hydrogen bonding between the hydroxyl group of methanol and the nitrogen atom of Schiff base has played a crucial role in the proton transfer process. It can be noted that in these dyads there is no any significant absorption band which cannot be assigned to specific individual subunits: this suggests that the interaction among the

various components is weak and attachment of the Schiff base fragment to the BODIPY entity causes minimal perturbation of its optical properties, so that these dyads can be regarded as multicomponent systems.

For a better understanding of the experimental data for the optical properties, the optimization of both keto and enol forms of 1 and 2 was carried out at the B3LYP/6-31+G(d,p) level using a polarizable continuum model (PCM) in the presence of methanol ($\varepsilon = 32.7$) (Table 2). Our theoretical results allow the conclusion that the total energy of the enol form of 1 obtained by the PCM method is still more stable than the keto form, though both HOMO and LUMO energy values become more and more negative in going from the gaseous phase to the solution phase with the increase of the dielectric constant value. However, calculated energies of 2 in methanol show that the enol-imine form is less stable than the keto-enamine form by $6.30 \text{ kJ} \text{ mol}^{-1}$, which indicates that it is energetically favorable to have carbon-carbon double bonds rather than carbon-nitrogen double bonds. In other words, the process of intramolecular proton transfer evoked by the influence of solvent results in destabilization of the OH form (a decrease in the prevalence of the OH form and an increase in that of the NH form) and destabilization of the aromatic form. Thus, the keto-enamine form of 2 is much more stable than enol-imine, which accounts for available UV-Vis experimental results.

Steady-state fluorescence spectra of 1 and 2 were also recorded in various solvents with increasing polarity from toluene to methanol, and the details are gathered in Table 2 and Fig. S9 (ESI[†]). From the viewpoint of fluorescence, the structures of BODIPY-linked Schiff bases can be composed of two fragments, the BODIPY moiety as a fluorophore and the Schiff base moiety as a fluorescence switch, which modulates the fluorescence quantum yield $(\Phi_{\rm fl})$ of the fluorophore, since they are orthogonal to each other. The starting material 3 was reported to display quenched emission in methanol with $\Phi_{\rm fl}$ < 1%.^{10e} The quenching phenomenon has all the hallmarks of photoinduced electron transfer (PET) from the phenylamino unit to the boradiazaindacene fluorophore. Upon condensation with salicylaldehyde to form 1, the reduction potential of the nonbonding electron pair on the nitrogen atom decreased due to the formation of an imine functional group. In other words, electron transfer from the electron-deficient imine moiety to the electron-rich BODIPY fluorophore became less feasible. The frontier orbital diagram also indicates that the highest occupied molecular orbital (HOMO) energy of the phenylamino unit (-5.38 eV) was higher than the HOMO energy of imine (-6.26 eV), thereby preventing PET quenching of the emission, exhibiting that the photoluminescence quantum efficiencies vary between 0.57 and 0.38 (Table 3).

In contrast, for 2, the value of $\Phi_{\rm fl}$ is up to 0.40 in toluene, and declines to only 0.05 in methanol. We speculate that the marked difference in fluorescence quantum yields between 1 and 2 in pure methanol is consistent in the prototropic tautomerism, and derives from an increase in the keto form for 2 compared with that of its analog 1. In order to experimentally strengthen the above speculation, the photo-physical properties of 2 had



Fig. 5 (a) Absorption spectra and (b) fluorescence spectra ($\lambda_{ex} = 470$ nm) of **2** in toluene-methanol mixtures with volume ratios of toluene; (c) photographs of the solutions of **2** in a mixture of the methanol-toluene solvent system with different toluene fractions under UV illumination.

been studied in a mixture of methanol-toluene, in which the toluene content (f_{toluene}) was varied in the range of 0–100 vol%. The UV-Vis spectra of 2 in the methanol-toluene solvent system showed several isosbestic points at 410, 364, and 324 nm, which definitely point out the existence of two molecular absorbing species in equilibrium (Fig. 5a). The luminescent properties of 2 were also investigated in the methanol-toluene system and the results are given in Fig. 5b. The emission intensity of 2 increased dramatically as the fraction of toluene f_{toluene} increased, and the logarithm of the intensity and the fraction have a good linear relationship with $R^2 > 0.99$ as shown in the inset of Fig 5b. The visual emission color of 2 in the methanol-toluene system when excited using a hand-held 365 nm UV lamp is shown in Fig 5c, which is consistent with the above analysis. Overall, these findings of fluorescence contrast with the above observations of UV-Vis spectra. Therefore, 1 retains a moderate fluorescence quantum yield while the lower value of $\Phi_{\rm fl}$ for 2 indicates a highly efficient fluorescence quenching by a thermodynamically allowed protoncoupled photoinduced electron transfer (PCPET) from the keto unit of NA to the singlet excited state of the BODIPY moiety.

To shed light on the photoinduced activation of an electron transfer process within an azomethine-BODIPY dyad, computations on 1 and 2 before and after prototropic tautomerism are also performed and displayed in Fig. S10 (ESI⁺) and Fig. 6. As shown in Fig. 6, before prototropic tautomerism of 2, the HOMO energy level of the enol form of the NA moiety (-6.26 eV) is obviously lower than that of the BODIPY unit (-5.78 eV), therefore, the PET process can be suppressed and the emission of the BODIPY fluorophore is on. The energy level of HOMO (-5.56 eV) of the keto form of the NA moiety should increase above that of the HOMO (-5.78 eV) of the fluorophore BODIPY only after prototropic tautomerism. Under these conditions, the electron transfer process becomes exergonic and favorable. As a consequence, when the BODIPY moiety of 2 is photoexcited, one electron can be transferred from the keto form of NA to the BODIPY moiety with a concomitant fluorescence quenching.

The calculated frontier molecular orbital (FMO) energies and surfaces of **2** are shown in Fig. 7. As can be found, both



Fig. 6 Proposed proton-coupled photoinduced electron transfer (PCPET) mechanism between the BODIPY moiety and the keto unit of 2.

the contours of the electronic distribution in HOMO and LUMO states of 2 in the enol form are located almost completely on the BODIPY moiety, while the HOMO - 1 and LUMO + 1 are located mainly on the NA fragment. It is postulated that the HOMO-LUMO transition corresponds to the emissive $\pi \rightarrow \pi^*$ excited state as observed in the reference dye TM-BODIPY and other BODIPY derivatives.¹⁰ As a result, the electronic transition between HOMO and LUMO for 2 in the enol form is limited only to the BODIPY moiety, leading to an intensive intrinsic fluorescence from the BODIPY moiety of 2 in the enol form. By contrast, the calculation results reveal that both the LUMO and HOMO -1 orbitals for 2 in the keto form are mostly contributed from the BODIPY moiety, while the HOMO and LUMO + 1 orbitals are mainly located at the NA fragment. The significant distribution difference between HOMO and LUMO of 2 in the keto form shows that there is electron transfer from the NA fragment (keto form) to the BODIPY core. And this is likely related to the PET process between the NA fragment (keto form) and the BODIPY core, which quenches the fluorescence of the BODIPY component.

2.5. Dyad 1 as an 'on-off' fluorescent chemosensor for Cu²⁺

Dyad **1** was preliminarily chosen to detect metal ions based on the following considerations: (1) as described in the foregoing discussion, **1** in the enol-imine state is the most stable form at room temperature in solution and shows moderate fluorescence quantum yields in most medium compared to dyad **2**. (2) Schiff bases are well known to be good ligands for metal ions, and Schiff bases incorporating a fluorescent moiety are appealing tools for optical sensing of metal ions.²²

Initially, the absorption and fluorescence response of 1 toward the nitrate salts of Cu^{2+} , Ag^+ , Al^{3+} , Ca^{2+} , Co^{2+} , Cr^{3+} ,



Fig. 7 Molecular orbital surfaces and energy levels given in parentheses for LUMO + 1, LUMO, HOMO, and HOMO -1 of enol and keto forms of 2 computed at the B3LYP/6-31+G(d,p) level in methanol solvent.

Fe³⁺, Li⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺, and Zn²⁺ were studied in a MeOH/CHCl₃ (20:1, v/v) solution (Fig. 8a and Fig. S11, ESI[†]). Changes in the fluorescence properties of 1 caused by various metal ions were measured once the emission intensity was constant. When 1 equiv. of Cu²⁺ was added to the solution of 1, the fluorescence intensity will be reduced by 80%, which suggested that 1 showed a particular response to Cu²⁺ ions compared to those of other metal ions of similar electronic structure. It is well-known that the paramagnetic Cu²⁺ center has a pronounced quenching effect on fluorophores through a photoinduced electron or energy transfer mechanism.²³ Additionally, among the relevant paramagnetic metal ions, Cu²⁺ has a particularly high thermodynamic affinity for ligands with N or O as the chelating element, and with a fast metal-to-ligand binding kinetic process.²⁴



Fig. 8 (a) Emission spectra of **1** (1.0×10^{-5} M) in the solution of MeOH/ CHCl₃ (20 : 1, v/v) upon addition of 3 equiv. of different metal nitrate salts; (b) fluorescent spectra of **1** (1.0×10^{-5} M, excited at 470 nm) upon addition of 0–1.0 equiv. of Cu²⁺.

Selectivity is a matter of necessity for a chemosensor. To investigate the selectivity of 1 for Cu^{2+} over other relevant cations, the fluorescence intensity changes upon addition of various competitive cations were examined, 3 equiv. of most other metal ions showed no interference to the sensing of Cu²⁺ by 1. Additionally, to explore the effects of anionic counterions on the sensing behavior of 1 to metal ions, fluorescence responses of 1 to chloride, nitrate, perchlorate and sulfate salts with Cu²⁺ were examined and it can be seen that anions had no influence on the fluorescence of 1 (Fig. S12, ESI⁺). The fluorescence intensity of 1 exhibits a gradual reduction upon the addition of 0–1.0 equiv. of Cu²⁺ and saturation upon the addition of 1.0–3.0 equiv. of Cu²⁺, revealing that the stoichiometry of the complex formed between 1 and Cu^{2+} ions is 1:1 (Fig. 8b). Overall, current preliminary experiments revealed that 1 can be potentially used as a simple fluorescent chemosensor which exhibited high selectivity for Cu²⁺ over other common cations. To further confirm the quenching mechanism, the coordination environment of the 1-Cu²⁺ complex and the corresponding association constant (K), more experiments including Job's method, ESI-MS, X-ray crystallography and NMR titration as well as DFT calculations are currently in progress.

3. Conclusions

Two new dyads made of azomethine and BODIPY subunits, 1 and 2, have been prepared, together with their parent species SA, NA and TM-BODIPY, and the photophysical properties of all the compounds have been investigated in fluid solution. Weak electronic interactions between Schiff base units and BODIPY fragments take place in the ground states of the two dyads, whose absorption spectra resemble those of their constituting groups. The marked difference in luminescence between 1 and 2 in methanol is observed and obviously consistent with the prototropic tautomerism of 2. Irradiation of dyad 2 in the enol state excites the BODIPY component, which then returns to its ground state by emitting light in the form of fluorescence. However, the keto state of 2 can donate an electron to the excited fluorophore. As a result of the protoncoupled photoinduced electron transfer (PCPET) process, the excited state of the BODIPY component is quenched and the associated fluorescence is suppressed. Theoretical calculations of total energies, potential energy surfaces (PESs) and the intrinsic reaction coordinate (IRC) analysis also support that the single proton transfer reaction from an enol form to a transition state (TS) and from the TS to the keto form for 2 is easier to occur than that for 1, which accounts for the fluorescence quenching phenomenon of 2. Additionally, 1 was preliminarily chosen as an on/off type fluorescent chemosensor for Cu²⁺ over other common cations.

This contribution not only attempts to integrate the fluorescent and tautomeric components within the same molecular skeleton, but also presents that the proton tautomerization can be designed to regulate the emission of an organic chromophore between a nonemissive state and an emissive one. In addition, in view of *ortho*-hydroxy aromatic Schiff bases exhibiting the interesting phenomenon of photochromism,²⁵ the detailed investigation of the relationship between fluorescence modulation and photochromic behavior of these azomethine–BODIPY dyads as well as other BODIPY-linked Schiff bases both in solution and in the solid state when exposed to light of different wavelengths is under progress in our laboratory.

4. Experimental

4.1. Materials

All the materials for the syntheses were purchased from commercial suppliers and used without further purification. Air- and moisture-sensitive reactions were carried out under a nitrogen atmosphere using oven-dried glassware. Solvents were dried by standard literature methods²⁶ before being distilled and stored under nitrogen over 3 Å molecular sieves prior to use. Water was deionized. Thin-layer chromatography (TLC) was performed using silica gel plates and flash column chromatography was conducted over silica gel (200–300 meshes) with the eluent reported in parentheses, both of which were obtained from the Qingdao Ocean Chemicals.

4.2. Instrumentation

¹H and ¹³C NMR spectra were recorded at room temperature using a Bruker PLUS 400 spectrometer with tetramethylsilane (TMS, 0.00 ppm) as an internal standard and CDCl₃ as a solvent. Chemical shift multiplicities are reported as s = singlet, d = doublet, and br = broad singlet. Coupling constant (J)values are given in Hz. Mass spectrometry (MS) experiment was carried out in the positive ion mode on a Bruker Esquire HCT ion trap mass spectrometer (Billerica, MA) coupled with a homemade electrospray ionization (ESI) device. Parameters of the ESI source were optimized to enhance the signal intensity. The pressure of nebulizing nitrogen, the flow rate of desolvation gas, and the temperature of desolvation gas were set to 8 psi, 1 L min⁻¹, and 250 °C, respectively. Electrochemical experiments were performed using a three-electrode system. The working electrode was 2 mm Pt with a Pt wire as an auxiliary electrode and a 0.01 M Ag/AgNO₃ solution as the reference electrode. The sample solution contained an azomethine-BODIPY dyad $(1.0 \times 10^{-3} \text{ M})$ and 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte in dry acetonitrile. FT-IR spectra were recorded from KBr pellets in the 4000-400 cm⁻¹ range on a Nicolet AVATAT FT-IR360 spectrometer. C, H, and N microanalyses were carried out using an EA 1110 analyzer from CE Instruments. The experimental powder X-ray diffraction patterns were recorded on a Panalytical X-Pert Pro diffractometer with Cu Ka radiation equipped with an X'Celerator detector. Differential scanning calorimetry (DSC) data were collected on a Netzsch-DSC-200F3 instrument at a heating rate of 10 °C min⁻¹ from 25 to 310 °C. Samples were heated in open aluminum pans under a nitrogen gas flow of 20 mL min⁻¹.

4.3. Spectroscopic measurements and determination of fluorescent quantum yields

Azomethine–BODIPYs were dissolved in various solvents to acquire optical measurements. Acetonitrile, methanol, tetrahydrofuran, dichloromethane and toluene were all individually used in preparing a BODIPY solution. UV-vis absorption and steady-state fluorescence spectroscopic studies are performed on a UV-2100 (Shimadzu) spectrophotometer and a F-7000 (Hitachi) spectrophotometer at room temperature. The slit width was 5 nm for both excitation and emission. Samples for absorption and emission measurements were contained in 1 cm \times 1 cm quartz cuvettes. Measurements were made using optically dilute solutions after deoxygenation by purging with dried N₂.

The relative fluorescence quantum yields ($\Phi_{\rm fl}^{\rm sample}$) of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of the standard. Only dilute solutions with an absorbance below 0.1 at the excitation wavelength $\lambda_{\rm ex}$ were used. The $\Phi_{\rm fl}^{\rm sample}$ values were calculated using synthesized 8-phenyl-4,4-difluoro-1,3,5,7-tetramethyl 4-bora-3*a*,4*a*-diaza-*s*-indacene (compound 3, $\Phi_{\rm fl}^{\rm standard} = 0.72$ in tetrahydrofuran)²⁷ as a fluorescence standard using the following equation:

$$\begin{split} \Phi_{\rm fl}^{\rm sample} &= \Phi_{\rm fl}^{\rm standard} \, \times \, \left(I^{\rm sample} / I^{\rm standard} \right) \times \, \left(A^{\rm standard} / A^{\rm sample} \right) \\ & \times \, \left(n^{\rm sample} / n^{\rm standard} \right)^2 \end{split}$$

where $\Phi_{\rm fl}^{\rm sample}$ and $\Phi_{\rm fl}^{\rm standard}$ are the emission quantum yields of the sample and the reference, respectively, $A^{\rm standard}$ and $A^{\rm sample}$ are the measured absorbances of the reference and the sample at the excitation wavelength, respectively, $I^{\rm standard}$ and $I^{\rm sample}$ are the area under the emission spectra of the reference and the sample, respectively, and $n^{\rm standard}$ and $n^{\rm sample}$ are the refractive indices of the solvents of the reference and the sample, respectively. The $\Phi_{\rm fl}^{\rm sample}$ values reported in this work are the average values of multiple (generally three), fully independent measurements.

4.4. Synthetic procedures

The syntheses of the starting BODIPY compounds NH_2 -BODIPY (3) and NO_2 -BODIPY (4) were achieved using literature methods and characterized by ¹H NMR, ¹³C NMR and elemental analysis to determine their structures.^{10e,12}

8-(4-Nitro-phenyl)-4,4-difluoro-1,3,5,7-tetramethyl 4-bora-3*a*,4*a*-diaza-*s*-indacene (4). ¹H NMR (400 MHz, CDCl₃) δ 1.37 (s, 6H), 2.57 (s, 6H), 6.03 (s, 2H), 7.54 (d, 2H, *J* = 8.8 Hz), 8.39 (d, 2H, *J* = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.5, 121.7, 124.4, 129.6, 130.6, 138.3, 141.9, 142.5, 148.4, 156.3. Anal. cacld for C₁₉H₁₈BF₂O₂N₃: C, 61.81; H, 4.91; N, 11.38. Found: C, 61.78; H, 4.87; N, 11.35.

8-(4-Amino-phenyl)-4,4-difluoro-1,3,5,7-tetramethyl 4-bora-3*a*,4*a*-diaza-s-indacene (3). ¹H NMR (400 MHz, CDCl₃) δ 1.51 (s, 6H), 2.57 (s, 6H), 4.44 (br, 2H), 5.99 (s, 2H), 6.86 (d, 2H, *J* = 4.0 Hz), 7.05 (d, 2H, *J* = 6.8 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 14.5, 14.6, 115.5, 119.7, 120.9, 124.7, 128.8, 128.9, 132.0, 142.6, 143.2, 146.9, 154.9. Anal. cacld for C₁₉H₂₀BF₂N₃: C, 67.28; H, 5.94; N, 12.39. Found: C, 67.33; H, 5.91; N, 12.31.

Synthesis of 8-(1-azastyryl(2-hydroxynaphthaldehyde))-4,4difluoro-1,3,5,7-tetramethyl 4-bora-3*a*,4*a*-diaza-*s*-indacene (2). 3 (339 mg, 1 mmol) and 2-hydroxy-1-naphthaldehyde (172 mg, 1 mmol) were refluxed for 6 h under a nitrogen atmosphere at 78 °C in 50 mL of absolute ethanol. When TLC analysis showed that the reaction was complete, the solution was cooled to room temperature. The product was collected by filtration as a red solid. Recrystallization from CH₂Cl₂–EtOH (356 mg, 75% yield); M.p. = 299 °C. ν_{max} (KBr pellet) cm⁻¹: 3442 (ν_{OH}), 1626 ($\nu_{C=N}$), 1600, 1576, 1548, 1511, 1466, 1408, 1359, 1309, 1257, 1201, 1155, 1117, 1091, 1073, 1038, 983, 893, 829, 803, 767, 744, 707, 506, 477. ¹H NMR (400 MHz, CDCl₃): 1.50 (s, 6H), 2.60 (s, 6H), 6.03 (s, 2H), 7.26 (d, *J* = 9.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 3H), 7.58 (dd, *J* = 17.0, 7.9 Hz, 3H), 7.78 (d, J = 7.9 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 9.48 (s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 14.62, 14.70, 74.34, 76.68, 77.00, 77.21, 77.32, 112.28, 116.48, 121.56, 121.87, 126.17, 127.82, 128.49, 129.17, 129.46, 130.92, 132.96, 135.60, 140.29, 148.04, 156.01. ESI-MS m/z (C₃₀H₂₆BF₂N₃O) calculated: 493.4, found: 516.3 (M + Na), 532.3 (M + K).

Synthesis of 8-(1-azastyryl(2-hydroxybenzaldehyde))-4,4difluoro-1,3,5,7-tetramethyl 4-bora-3a,4a-diaza-s-indacene (1). 3 (339 mg, 1 mmol) and 2-hydroxy-1-benzaldehyde (125 mg, 1 mmol) were refluxed for 6 h under a nitrogen atmosphere at 78 °C in 50 mL of absolute ethanol. When TLC analysis showed that the reaction was complete, the solution was cooled to room temperature. The product was collected by filtration as an orange solid. Recrystallization from CHCl3-EtOH (300 mg, 80% yield); M.p. = 288 °C. ν_{max} (KBr pellet) cm⁻¹: 3441 (ν_{OH}), 1623 ($\nu_{\text{C=N}}$), 1597, 1573, 1545, 1508, 1467, 1409, 1365, 1306, 1279, 1195, 1154, 1120, 1086, 1052, 978, 910, 842, 810, 761, 708, 665, 581, 479. ¹H NMR (400 MHz, CDCl₃): δ 1.48 (s, 6H), 2.59 (s, 6H), 6.03 (s, 2H), 7.00 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.41–7.49 (m, 4H), 8.74 (s, 1H), 13.08 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.75, 14.64, 76.71, 77.02, 77.23, 77.34, 117.40, 119.03, 119.29, 121.35, 122.00, 129.09, 129.32, 131.46, 132.51, 133.58, 133.66, 140.95, 143.00, 149.10, 155.71, 161.26, 163.45. ESI-MS m/z (C26H24BF2N3O) calculated: 443.3, found: 466.3 (M + Na), 482.3 (M + K).

8-Phenyl-4,4-difluoro-1,3,5,7-tetramethyl 4-bora-3*a*,4*a*-diaza*s*-indacene (5). 5 was synthesized according to the literature reports.¹⁵ ¹H NMR (400 MHz, CDCl₃) δ 1.39 (s, 6H, CH₃), 2.58 (s, 6H, CH₃), 6.00 (s, 2H), 7.28–7.32 (m, 2H, phenyl), 7.49–7.50 (m, 3H, phenyl); ¹³C NMR (100 MHz, CDCl₃) δ 14.3, 14.6, 121.2, 127.9, 128.9, 129.1, 131.4, 135.0, 141.7, 143.1, 155.4. Anal. cacld for C₁₉H₁₉BF₂N₂: C, 70.40; H, 5.91; N, 8.64. Found: C, 70.44; H, 5.88; N, 8.67. Since 5 is an internal reference dye for the determination of quantum yields it is regularly checked for stability and purity.

4,4-Difluoro-1,3,5,7-tetramethyl 4-bora-3*a*,4*a*-diaza-s-indacene (the model TM-BODIPY). TM-BODIPY was prepared using a literature procedure.^{19 13}C NMR (125 MHz, CDCl₃) δ 11.3, 14.6, 119.1, 120.2, 133.3, 141.2, 156.7. ESI-MS *m*/*z* (C₁₃H₁₅BF₂N₂) calculated: 248.1, found: 271.1 (M + Na).

References N-salicylideneaniline (SA) and N-naphthlideneaniline (NA) are synthesized by the appropriate condensation of the

corresponding aldehyde and aniline according to the standard procedures as previously reported.^{8c,28} Pure SA and NA were obtained after recrystallization twice from absolute ethanol. The melting points agreed with those in the literature and the elemental analyses were in accord. Other analysis data are as follows. SA: M.p. 51–53 °C. ¹H NMR(400 MHz, CDCl₃): δ 6.98 (q, 1H, J = 7.3 Hz), 7.09 (d, 1H, J = 8.3 Hz), 7.33 (m, 3H), 7.45 (m, 4H), 8.67 (s, 1H). FT-IR transmission (KBr pellet): 3433 cm^{-1} $(\nu_{\rm OH})$, 1615 cm⁻¹ $(\nu_{\rm C=N})$, 1590, 1572, 1507, 1496, 1485, 1453, 1402, 1361, 1277, 1186, 1169, 1150, 1116, 1074, 1032, 982, 917, 896, 843, 780, 757, 691, 547, 523 cm⁻¹. UV-Vis, λ_{max}/nm , $(\varepsilon/L \text{ mol}^{-1} \text{ cm}^{-1})$, (CH₃OH): 269 nm (11000), 348 nm (10570). Anal. calcd for C13H11NO (197.23): C, 79.17; H, 5.62; N, 7.10. Found: C, 79.12; H, 5.57; N, 7.02. NA: M.p. 95-97 °C. ¹H NMR(400 MHz, CDCl₃): δ 7.14 (d, 1H, J = 9.12 Hz), 7.37 (d, 2H, J = 8.52 Hz), 7.44 (m, 2H, J = 13.48 Hz), 7.71 (d, 1H, *J* = 7.93 Hz), 7.80 (d, 1H, *J* = 9.11 Hz), 8.07 (d, 1H, *J* = 8.59 Hz). FT-IR transmission (KBr pellet): 3437 cm⁻¹ (ν_{OH}), 1626 cm⁻¹ $(\nu_{C=N})$, 1570, 1542, 1489, 1476, 1420, 1329, 1248, 1181, 1163, 1076, 1023, 967, 911, 873, 824, 750, 694 cm⁻¹. UV-Vis, λ_{max}/nm , $(\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1})$, (CH₃OH): 315 nm (17283), 357 (12228), 435 nm (22000) and 455 nm (20400). Anal. cacld for C₁₇H₁₃NO (247.3): C, 82.57; H, 5.30; N, 5.66. Found: C, 82.61; H, 5.35; N, 5.55.

4.5. Crystallization experiments and X-ray crystallography

The quality of single crystals depends on the purity of the used material. Hence, the synthesized target dyads were highly purified (recrystallization at least twice before performing crystallization experiments). Better quality crystals of **1** and **2** were obtained by slow vapour diffusion of *n*-hexane into a saturated CHCl₃ solution of **1** or CH₂Cl₂ solution of **2** at room temperature.

Intensity data for 1 and 2 were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer using a graphitemonochromated Mo K α radiation source ($\lambda = 0.71073$ Å). Single crystals of 1 and 2 with appropriate dimensions were chosen under an optical microscope and mounted on a glass fiber for data collection at low temperature (173 \pm 2 K). Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.²⁹ All structures were solved by direct methods using SHELXS-97³⁰ and refined by fullmatrix least-squares on F^2 using SHELXL-97³¹ via the program interface X-Seed.³² Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to oxygen in 1 and 2 were located using difference Fourier maps and other hydrogen atoms were refined isotropically using a riding model with Uiso values 1.2-1.5 times those of their parent atoms. All structures were examined using the Addsym subroutine PLATON³³ to ensure that no additional symmetry could be applied to the models. Crystal structure views were obtained using Diamond v3.1.34 Details of the data collection conditions and the parameters of the refinement process are given in Table S2 (ESI[†]). Selected bond lengths and angles are listed in Table S3 (ESI⁺). The hydrogen bond geometries for 1 and 2 are shown in Table 1.

4.6. Computational details

Theoretical calculations have been performed using the Gaussian 09 software package.³⁵ For the purpose of accordance with experimental results, the molecular structures of 1 and 2 are taken from the crystal structures before optimization. The geometry optimization of enol and keto forms as well as the transition states (TS) of 1 and 2 in the gas phase is performed by carrying out density functional theory (DFT) calculations using Becke's three-parameter exchange and Lee-Yang-Parr correlation functionals (B3LYP) with a combination of the 6-31+G(d,p)basis set. The harmonic vibrational frequencies of the studied structures are calculated at the same level to characterize their existence on the potential energy surface (PES). The minimum energy structures are ensured by the absence of any imaginary frequency whereas any transition state is characterized by the presence of only one imaginary frequency. In the solution phase, the geometry optimization of the studied structures is performed at the same level using a polarizable continuum model (PCM). All molecular orbitals were visualized using the software GaussView 5.0.

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of bonds in the ring, R_i is an individual bond length, α_i is an empirical constant equal to 257.7 and R_{opt} is equal to 1.388 Å for CC bonds. For purely aromatic compounds, HOMA index is equal to 1 while it is equal to 0 for nonaromatic compounds. See: (*a*) T. M. Krygowski, *J. Chem. Inf. Comput. Sci.*, 1993, **33**, 70–78; (*b*) T. M. Krygowski and M. K. Cyrański, *Chem. Rev.*, 2001, **101**, 1385–1419.

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