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Visualized acid-base discoloration and optoelectronic investigations for azines and azomethines having double 4-[N,N-di(4-methoxyphenyl)amino]phenyl terminals

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Two small molecular chromogenic sensors (azine **MS-1** and azomethine **MS-2**) were synthesized for the acid-base discoloration and optoelectronic investigations. It was found that the color of both sensors in solution and in the solid state changed obviously from yellow to purple and blue after the treatment with an acid, which could be easily detected by the naked eye. Furthermore, single-crystal conductance of **MS-1** and **MS-2** could be significantly enhanced after treating with the flow of HCl gas. On the other hand, **MS-2** showed relatively good film-forming ability and could be used as a hole transport material (HTM) in perovskite solar cells, exhibiting a power conversion efficiency (PCE) of 6.68 %. To the best of our knowledge, this is the first demonstration of perovskite solar cells including a HTM based on a low-cost Schiff-base structure.

Introduction

In recent years, π -conjugated organic semiconducting compounds with well-defined structures have drawn attention as materials for a variety of electronic and optoelectronic devices such as organic and polymeric light emitting diodes,1 field effect transistors,2 and photovoltaic cells.³ Among the π -conjugated compounds, azines having N-N linked diimines (R-CH=N-N=CH-R) and azomethines bearing imine linkages (-CH=N-), are found to be good candidates for multifunctional materials.⁴ Interestingly, their electron distribution can be tuned by protonation with Lewis acids and complexation with Bronsted acids. The optical properties of a molecule are strongly dependent on its electron distribution. Thus, Schiff bases containing azine or azomethine units can be used for reversible acid-base discoloration investigation.5 In most of the common designs, pH probes rely on weak acidic dyes whose dissociated and undissociated forms have different absorption or emission maxima.⁶ However, acid-base discoloration based on Schiff bases has been less reported.5,7 On the other hand, azomethines exhibit high chemical, oxidative, and reductive resistance and interesting photophysical properties.8 They are also possible alternatives to butadiene linkages which could be used as cost-effective hole transport material (HTM) in perovskite solar cells.9

In our previous work, some azo dyes have been studied on the azo-hydrazone tautomerism, which is evidenced by UV-Vis spectra using pH-titration.¹⁰ Furthermore, a series of thiazole-based and

oligothiophene-based heterocyclic aromatic compounds with terminal thienyl, pyridyl and triphenylamino groups has been described.¹¹ The current work is the combination of our efforts in the studies of organic materials for possible applications in acid-base discoloration and organic optoelectronics, where two compounds bearing double 4-[N,N-di(4-methoxyphenyl)amino]phenyl terminals (azine MS-1 and azomethine MS-2 as shown in Scheme 1) have been prepared. It is found that their UV-Vis absorption and fluorescence emission change observably when adding trifluoroacetic acid ($p[TFA] = -\log c[TFA]$). It is also noted that the single-crystal conductance of MS-1 can be significantly improved from $1.64 \times 10^{-5} \text{ S} \cdot \text{m}^{-1}$ to $1.58 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ after being treated with hydrochloric acid gas. Furthermore, the introduction of electrondonating 4-[N,N-di(4-methoxyphenyl)amino]phenyl groups could effectively increase the highest occupied molecular orbital (HOMO) levels of MS-2, which makes it a good candidate as HTM for perovskite solar cells.



Scheme 1 Synthetic route to azine MS-1 and azomethine MS-2.

Results and discussion

Single-crystal structures and thermal stability

Single-crystal structures of both azine **MS-1** and azomethine **MS-2** were successfully obtained to fully characterize their molecular geometry. As depicted in Fig. 1, **MS-1** has good molecular planarity with zero dihedral angle between two phenyl rings at each side of azine unit because the central azine unit lies on an inversion centre. In contrast, there are two crystallographically independent molecules in the asymmetric unit cell of **MS-2**, and the dihedral angles between two phenyl rings at each side of azomethine unit are different at 5.9(7) and 45.3(4)°, respectively.



Fig. 1 ORTEP drawings of **MS-1** (a) and **MS-2** (b) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level and all the hydrogen atoms are omitted for clarity.

Thermal durability of small molecules is one of the most essential parameters for the organic optoelectronic applicability.¹² In this work, compounds **MS-1** and **MS-2** have been checked by the thermo gravimetric analysis (TGA) measurements, and a parameter of Td_{10} (10 % weight-loss temperature) is used to describe the thermal stability of these compounds. As shown in Fig. SI1, they exhibit similar TGA curves where the Td_{10} values for them are found to be 320 °C indicative of relatively high thermal stability of **MS-1** and **MS-2**.

pH-Dependent optical properties

UV-Vis spectra of **MS-1** and **MS-2** were recorded in the dichloromethane solutions with the same concentration of 1.0×10^{-5} M. Acid-base discoloration experiments were carried out by adding different amounts of TFA to their dichloromethane solutions at room temperature. Both dyes in dichloromethane solution show similar spectral behavior (black curves in Fig. 2a and 2b). There are three absorption peaks centered at 290, 372 and 417 nm ($\varepsilon = 2.91, 3.46$

and $2.77 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$) in **MS-1**, and 299, 356 and 410 nm ($\varepsilon = 3.00, 3.47$ and $2.59 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$) in **MS-2**.

However, a new absorption peak centered at 520 nm is observed in MS-1 by adding TFA, accompanying with the decreasing of absorptions for above-mentioned three peaks to different extents. Furthermore, the strength of this new peak at 520 nm increases with the amount of added TFA, and even overwhelms all the other three original absorption peaks when the concentration of TFA equals to 0.1 M ($\varepsilon = 3.14 \times 10^4$ M⁻¹ cm⁻¹). At the same time, the color of solution changes remarkably from yellow to purple, which can be easily detected by the naked eye. With regard to MS-2, a new absorption peak can also be found at around 520~550 nm with weaker absorption strength. Different from MS-1 with only one isoabsorptive point at 450 nm, two isoabsorptive points are observed at 450 and 571 nm for MS-2, respectively, and they can be shifted to each other with the alteration of p[TFA] values. That is to say, the isoabsorptive point at 450 nm in MS-2 corresponds to p[TFA] > 3, while it is red-shifted to 571 nm when the p[TFA] values are less than 3. Accompanied by the shift of isoabsorptive point, the color of solution changes from yellow to purple and blue accordingly, exhibiting visualized acid-base discoloration behavior. As shown in Fig. SI2a, the detection linear range of MS-1 for TFA was determined to be $2.0 \times 10^{-3} \sim 0.1$ M with the detection limit of $5.0 \times 10^{-3} \sim 0.1$ M with the detection limit of 10⁻⁴ M. With regard to **MS-2**, the detection linear range for TFA was determined to be $1.0 \times 10^{-7} \sim 1.0 \times 10^{-3}$ M, indicating that **MS-2** is more sensitive to acid than MS-1.



Fig. 2 UV-Vis absorption vs p[TFA] spectra of MS-1 (a) and MS-2 (b) in their CH₂Cl₂ solutions with the same concentration of 1.0×10^{-5} M at room temperature.

Considering the presence of one and two isoabsorptive points for azine MS-1 and azomethine MS-2 in their acid-base discoloration experiments as well as their molecular structures, suppositional equilibriums are given for each of them. We suggest the visualized acid-base discoloration is originated from one-step or two-step protonation process of Schiff base units in the molecular structures of MS-1 and MS-2. It is known that Schiff bases contain available active centers for proton attacks and their electron distribution can be tuned by protonation. Accordingly, the $n-\pi^*$ and $\pi-\pi^*$ transitions within the molecules can be greatly influenced by the addition of TFA in this work. As illustrated in Scheme 2, three quinone structures $MS-1^{2+}$, $MS-2^{+}$ and $MS-2^{2+}$ are suggested to be formed by adding different amounts of TFA and they are in equilibrium with MS-1 and MS-2, and the two isoabsorptive points observed in the UV-Vis of MS-2 spectra could be assigned as two phases (I↔II and II↔III), respectively.



Scheme 2 The suppositional equilibriums between MS-1, MS-2 and their protonated quinone structures MS-1²⁺, MS-2⁺, MS-2⁺.



Fig. 3 Comparative 1 H NMR spectra for MS-1 and its TFA adduct (MS-1+TFA).

In the ESI-MS spectra, **MS-1** and **MS-2** have the molecular ion peaks at m/z = 663 and 636 in 100 % abundance, and the molecular ion peaks retain unchanged after adding excess TFA, indicating that they are stable in acidic solution. To further reveal the suppositional equilibrium, comparative ¹H NMR spectra for **MS-1**, **MS-2** and their TFA adducts have been recorded, as shown in Fig. 3 and SI4. As for **MS-1**, it is found that the single peak assigned as two protons of the

CH=N units is shifted to higher field from 8.537 to 8.376 ppm after the addition of TFA. In addition, half of four benzene protons between the azine unit and nitrogen atoms of the terminals, which are close to the latter, are shifted to higher field from 6.898 and 6.880 ppm to 6.850 and 6.833 ppm. On the contrary, all the other four groups of protons of MS-1 are found to move to lower field to different extents. It is worth mentioning that the change of the chemical shifts for the imine protons is the largest one for both of MS-1 and MS-2 before and after the addition of TFA. In addition, the fluorescence spectrum exhibits a strong emission peak at 520 nm in the case of MS-1. This peak is red-shifted by 25 nm in comparison with a similar compound (AZ-5) reported by Ewa Schab-Balcerzak *et al*⁷ in the absence of electron-donating methoxyl groups. It is also found that significant fluorescence reduction is observed after the addition of TFA into the MS-1 solution (Fig. SI5), while MS-2 is found to be fluorescence inactive by contrast.

Single-crystal conductance



Fig. 4 I-V curves and solid UV-Vis spectra (Inset) for **MS-1** and its hydrochloric adduct at room temperature, together with the photos of single-crystal samples before and after the treatment with the flow of HCl gas.

Moreover, alteration on the solid-state conductance of MS-1 before and after being treated with the flow of HCl gas has been made, where two ends of single-crystal samples of MS-1 and its hydrochloric adduct were covered by a pair of electrodes made of conductive silver paste. Each I-V curve was recorded between the pair of electrodes, respectively, by means of a four-probe system under the same experimental conditions. As displayed in Fig. 4, the average conductance obtained from linear fitting of the I-V curves reveal about ten times' enhancement after being treated with hydrochloric acid gas, namely varying from 1.64×10^{-5} to 1.58×10^{-5} 4 S·m⁻¹. It is easy to see that the change of solid UV-Vis spectra after the treatment with hydrochloric acid gas was almost the same with the experiment of acid-base discoloration in dichloromethane solution. According to the experimental results, the enhancement of conductance may be owing to the formation of MS-1²⁺ ion in the solid state, because the hydrochloric adduct of MS-1 is a protonated species and it has better electron transmission ability than MS-1. As for MS-2, the conductance also exhibits significant enhancement from 8.96×10^{-6} to 8.06×10^{-5} S·m⁻¹ after treating with TFA (Fig. SI6). The result reveals that the variation of single-crystal conductance caused by acidification is a general character for this

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class of Schiff base compounds.

Density functional theory (DFT) calculations



Fig. 5 Frontier orbitals of MS-1, MS-1²⁺, MS-2, MS-2⁺ and MS-2²⁺.

To further reveal the characteristics of π -conjugated dyes, the optimized molecular structures for MS-1, MS-1²⁺, MS-2, MS-2⁺ and $MS-2^{2+}$, together with the frontier molecular orbitals of their calculated HOMOs and lowest unoccupied molecular orbitals (LUMOs), are shown in Fig. 5. All calculations were performed with the Gaussian 09 program package,13 employing the DFT method with Becke's three parameter hybrid function and Lee-Yang-Parr's gradient corrected correlation function (B3LYP). The fixed atom coordinates of MS-1 and MS-2, originating from the structural parameters determined by the X-ray diffraction method, were used as the input files for the ground state optimization. DFT calculations manifest that the HOMO orbitals of MS-1 and MS-1²⁺ are located on the whole molecule skeleton while LUMO orbitals are located on the central azine units. Similarly, the LUMO orbitals of MS-2, MS- 2^+ and MS- 2^{2+} are located on the central azomethine units. This is the same as the case of Spiro-OMeTAD, where the LUMO localizes on the central spiro-group.¹⁴ Nevertheless, the HOMO orbital of MS-2²⁺ is mainly located on 4-[N,N-di(4methoxyphenyl)amino]phenyl terminal away from the protonated side, which is found to shift towards the other side of divalent cation compared with those in MS-2 and MS-2⁺. It is known that the introduction of electron-donating 4-[N.N-di(4methoxyphenyl)amino]phenyl groups into our molecules could effectively increase the HOMO levels. Actually, the calculated hole reorganization energies (λ_{hole}) of these Schiff-base materials (170 meV for MS-1 and 203 meV for MS-2) are close to the typical HTM Spiro-OMeTAD (148 meV),¹⁵ showing potential of MS-1 and MS-2

as hole-transporting materials in perovskite-based solar cells.

Moreover, UV-Vis spectra of MS-1, MS-1²⁺, MS-2, MS-2⁺ and MS-2²⁺ were calculated, respectively, by using the TD-DFT method according to abovementioned optimized geometries (Fig. SI7). In comparison with MS-1, a new band at 800 nm is produced in MS-1²⁺, accompanying with the decrease of absorptions for the other peaks between 200 and 600 nm. Analogously, a new absorption band can also be found at around 700 nm in MS-2⁺ compared with that in MS-2. In addition, as for divalent cation MS-2²⁺, the band at around 700 nm in is weaker than that in MS-2⁺. On the contrary, the band at around 400~500 nm in MS-2⁺ is much stronger than that in MS-2⁺. It is concluded that the calculated UV-Vis spectra of MS-1, MS-1²⁺, MS-2, MS-2⁺ and MS-2²⁺ are in good agreements with the experimental results, indicating that the suppositional equilibriums in Scheme 2 are acceptable.

Optoelectronic properties

recently, hybrid organic-inorganic Verv perovskites (CH₃NH₃PbX₃, where X corresponds to halogens) have been introduced as light harvesters in low-cost solar cells.¹⁶ Power conversion efficiencies (PCE) of exceeding 15 % have been reported with $CH_3NH_3PbI_{3-x}Cl_x$ as light absorber and 2,2',7,7'-tetrakis(N,Ndi-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) as the HTM.¹⁷ Nevertheless, Spiro-OMeTAD is expensive because of its tedious synthetic methodology even if it is found to be the most effective small-molecule HTM for perovskite solar cells. Lots of efforts have been taken to develop a cheaper alternative to replace Spiro-OMeTAD, such as pyrene arylamine derivatives¹⁸ and butadiene derivatives.^{9,19} However, effective perovskite solar cells based on Schiff-base HTMs have never been reported.



Fig. 6 Cyclic voltammetry (a) and differential pulse voltammetry (b) curves of MS-1, MS-2 and Spiro-OMeTAD recorded in 1.0×10^{-3} M solutions of tetrabutylammonium perchlorate in CH₂Cl₂.

As depicted in Fig. 6, the electrochemical behavior of **MS-1**, **MS-2** and Spiro-OMeTAD was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH₂Cl₂ solution (1.0 × 10⁻³ M) containing 0.1 M TBAClO₄ as the supporting electrolyte. All potentials reported herein were calibrated with the ferrocene/ferrocenium couple (F_c/F_c^+) as the internal standard reference. Oxidation onset potentials (E_{ax}^{onset}) as well as HOMO and LUMO energy levels were determined by the DPV and UV-Vis absorption data. The onset oxidation was evaluated relative to the F_c/F_c^+ couple, where an energy level of -5.10 eV versus vacuum was assumed.²⁰ As shown in Fig. 7, the HOMO levels of **MS-1** and **MS-2** were estimated to be are -5.38 and -5.24 from DPV measurements, respectively. Compared with AZ-5,⁷ the introduction of four electron-donating methoxyl groups could effectively decrease the Journal Name

initial oxidation potential of compound MS-1 from 0.55 to 0.28 V. The reported HOMO energy level for $CH_3NH_3PbI_3$ was -5.44 eV,¹⁸ which indicated that both the two compounds have energetics favorable for the hole transfer. So the HOMO energy of **MS-2** is more similar with that of Spiro-OMeTAD and it is used for perovskite solar cells fabrication. In contrast, **MS-1** displays very poor film-forming ability, and it is difficult for us to get reliable and reproducible devices.



Fig. 7 Energy level diagram of the materials used in perovskite solar cells.



Fig. 8 (a) Current-voltage curves of typical small-area (0.09 cm²) perovskite solar cells based on MS-2 and Spiro-OMeTAD under the AM1.5 simulated sunlight (100 mW cm⁻²) illumination. (b) Incident photon-to-current conversion efficiencies of the photovoltaic devices based on MS-2 and Spiro-OMeTAD.

The **MS-2** based device gave $J_{sc} = 13.46 \text{ mA} \cdot \text{cm}^{-2}$, $V_{oc} = 0.78 \text{ V}$ and FF = 0.56, affording power conversion efficiency (PCE) = 6.68 %, as can be seen in Table 1. The blank experiments using Spiro-OMeTAD gave $J_{sc} = 18.16 \text{ mA} \cdot \text{cm}^{-2}$, $V_{oc} = 0.85 \text{ V}$ and FF =0.68, corresponding to the PCE of 10.51 %. The photocurrent action spectra of the two devices are presented in Fig. 8a. The incident photon-to-current conversion efficiencies (IPCEs) of the perovskite solar cells are shown in Fig. 8b. As depicted in Fig. SI8, the device fabricated with Spiro-OMeTAD presented an obviously longer lifetime compared to that fabricated with MS-2. The result was consistent with the observed shift in the $V_{\rm OC}$ value under standard global AM1.5 illumination. On the other hand, the low FF value of device based on MS-2 can partly be explained by the high series resistance (R_s) compared with that of Spiro-OMeTAD. In addition, the hole mobility determined by using the space charge limited current method²¹ gave a value of 8×10^{-6} cm²·V⁻¹·s⁻¹ for MS-2 (Fig. SI9). The lower hole mobility of MS-2 relative to Spiro-OMeTAD $(2 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})^{21}$ is also responsible for the decrease of fill factor and PCE of the perovskite solar cell. Although the measured PCE based on MS-2 is lower than the device based on Spiro-OMeTAD, it is still valuable to the research of solar cells taking its relative ease of synthesis into account.

Table 1	Photovoltaic	performance	of perovskite	solar cells	based on HTMs
		1			

HTM	$E_{\rm HOMO}^{a}$	E_{LUMO}	$J_{ m sc}$	$V_{\rm oc}$	FF^{b}	η (%)	Rs	
	(eV)	(eV)	$(mA \cdot cm^{-2})$	(V)			(Ω)	
Spiro-	-5.22	-2.27	18.16	0.85	68.1	10.51	29.31	
OMeTAD								
MS-2	-5.24	-2.76	13.46	0.78	56.2	6.68	52.38	
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^a E_{HOMO} and E_{LUMO} were calculated with the following formula: HOMO (eV) = E_{ox} - $E_{Fe/Fc}^{++}$ + 5.10; LUMO (eV) = HOMO - E_g . E_g is the absorption onset estimated from the electronic absorption spectra of the sensitizers; ^b FF = fill factor.

Experimental

Materials and measurements

All reagents were purchased from commercial suppliers and used as received. 4-[Bis(4-methoxyphenyl)amino]benzaldehyde and 4amino-4',4"-dimethoxytriphenylamine were prepared according to the literature methods.^{22,23} Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. UV-Vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. ¹H NMR spectra were obtained on a Bruker AM-500 NMR spectrometer, using TMS (SiMe₄) as an internal reference at room temperature. Electrospray ionization mass spectra (ESI-MS) were recorded by a ThermoFisher Scientific LCQ Fleet mass spectrometer in a scan range of 100-2000 amu. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Cyclic and differential-pulse voltammetry were performed with a CHI660D instrument, using a Pt disk as the working electrode, platinum wire as the auxiliary electrode with porous ceramic wick, Ag/Ag^+ as the reference electrode, standardized for the redox couple of ferricinium/ferrocene. Photovoltaic measurements were recorded with a Newport Oriel solar simulator (Model 91160) equipped with a class a xenon light source powered by a Newport power supply. The power output of the lamp was measured to 1 Sun (100 mW cm^{-2}) using a certified Si reference cell. The current-voltage (I-V) curves of every cell were obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley digital source meter (Model 2400). IPCE measurements were performed on a Newport QE measurement system (Model 70104).

Solar cell fabrication: Fluorine doped tin oxide (FTO) glass was etched with zinc powder and diluted HCl solution, the etched substrates were cleaned by ultrasonication using decon-soap solution, deionized water and ethanol, followed by O_3/UV treatment. The compact TiO₂ underlayer (30 nm) was deposited by aerosol spray pyrolysis on the FTO surface at 500 °C using 6 mL of a titanium diisopropoxidebis(acetylacetonate) solution (75 % in 2-propanol) diluted in ethanol (1:39, v/v) and oxygen as carrier gas, and sintered on a hot plate for 1 h at 500 °C. Porous TiO₂ films of 200 nm thick were deposited onto compact layer covered substrates by spin coating at 5000 r.p.m. for 30 s using a TiO₂ paste (Dyesol 30NRD, 30 nm average particle size) diluted in anhydrous ethanol (1:3, weight ratio). After drying at 120 °C, the TiO₂ layers were heated to 470 °C for 15 min. The prepared mesoporous TiO₂ films were infiltrated with a solution of PbI₂ in *N*,*N*-dimethylformamide (508 mg/1 mL) by spin coating at 8000 r.p.m. for 90 s and dried at 70 °C for 30 min. After cooling to room temperature, the resulted TiO₂/PbI₂ composite film was dipped into a solution of CH₃NH₃I in 2-propanol (10 mg/mL) for 30 s. The resulting perovskite film was washed with dry 2-propanol and N₂ flow, dried at 70 °C for 30 min. The HTMs were coating via solution process by following details. Spiro-OMeTAD/chlorobenzene (180 mg/1 mL) and **MS-**2/chlorobenzene (72 mg/1 mL) solutions with additives containing 17.5 µL Li-TFSI)/acetonitrile (520 mg/1 mL) and 28.8 µL TBP were spin-coated on CH₃NH₃PbI₃/mp-TiO₂/bl-TiO₂/FTO substrate at 4000 r.p.m. for 30 s. Finally, 65 nm of gold was thermally evaporated in the vacuum chamber on top of the device to form the electrode contacts. The device fabrication was carried out under controlled atmospheric conditions and a humidity of < 1.0 ppm.

Synthesis

Compound MS-1: 85 % Hydrazine hydrate (0.059 g, 1.0 mmol) was added dropwise to a solution of 4-[bis(4methoxyphenyl)amino]benzaldehyde (0.667 g, 2.0 mmol) in acetic acid (20 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography over silica gel using hexane/CH₂Cl₂ (v/v = 1:1) as the eluent to give 0.278 g (42 %) of MS-1 as a light yellow solid. Mp: 85-87 °C. ¹H NMR (CDCl₃, 500 MHz, ppm) δ : ¹H NMR (500 MHz, CDCl₃) δ 8.54 (s, 2H), 7.60 (d, J = 8.7 Hz, 4H), 7.10 (d, J = 8.8 Hz, 8H), 6.89 (dd, J = 15.6, 8.8 Hz, 12H), 3.81 (s, 12H). Positive ESI-MS in methanol (m/z): 663.6 [M]⁺. Anal. Calcd. for C23H15NOS: C, 76.11; H, 5.78; N, 8.45 %;. Found: C, 76.01; H, 5.97; N, 8.24 %.

Compound **MS-2**: 4-Amino-4',4"-dimethoxytriphenylamine (0.640 g, 2.0 mmol) was added dropwise to a solution of 4-[bis(4-methoxyphenyl)amino]benzaldehyde (0.667 g, 2.0 mmol) in acetic acid (20 mL). The reaction mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography over silica gel using hexane/CH₂Cl₂ (v/v = 1:1) as the eluent to give 0.762 g (60 %) of **MS-2** as a light yellow solid. Mp: 80-82 °C. ¹H NMR (CDCl₃, 500 MHz, ppm) δ : ¹H NMR (500 MHz, CDCl₃) 8.35 (s, 1H), 7.64 (dd, *J* = 11.3, 8.8 Hz, 2H), 7.15-7.07 (m, 6H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.99-6.77 (m, 14H), 3.85-3.76 (m, 12H). Positive ESI-MS in methanol (*m/z*): 636.7 [M]⁺. *Anal. Calcd.* for C₂₃H₁₅NOS: C, 77.46; H, 5.87; N, 6.61 %; Found: C, 77.21; H, 6.02; N, 6.45 %.

X-ray data collection and solution

Single-crystal samples of **MS-1** and **MS-2** were covered in glue and mounted on glass fibers for data collection on a Bruker SMART 1K CCD area detector at 123(2) K, using graphite mono–chromated Mo K*a* radiation ($\lambda = 0.71073$ Å). The collected data were reduced by using the program SAINT²⁴ and empirical absorption corrections were done by SADABS²⁵ program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences by using XPREP. The structures were solved by direct method and refined by least-squares method. All non-hydrogen atoms were refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters. All the hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. All calculations were carried out with the SHELXTL PC program package.²⁶

Conclusions

summary, protonation-triggered visualized acid-base In discoloration studies have been described for azine MS-1 and azomethine MS-2. According to the experimental evidences and related analyses on UV-Vis and ¹H NMR spectra, we come to a conclusion that the protonation/deprotonation equilibriums for MS-1 and MS-2 may lead to the acid-base discoloration. Single-crystal structures of MS-1 and MS-2 are included and single-crystal conductance of MS-1 and MS-2 could be significantly enhanced (~ 10 times) after being treated with the flow of HCl gas. On the other hand, MS-2 can be used as a HTM in perovskite solar cells exhibiting a PCE of 6.68 %. As far as we are aware, this is the first report that a low-cost Schiff base is used as the HTM in perovskite solar cells.

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Notes and references

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Visualized acid-base discoloration and optoelectronic investigations for azines and azomethines having double 4-[*N*,*N*-di(4-methoxyphenyl)amino]phenyl terminals

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Graphic Abstract



MS-1 and **MS-2** exhibit visualized acid-base discoloration and **MS-2** could be used as a low-cost HTM in perovskite solar cells.