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Spiropyran-azobenzene-DBU System as Solvent Indicator

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Abstract: A dyad bearing azobenzene and spiropyran units was synthesized and its applications in indicating the polarity and protic or aprotic properties of a solvent were explored. The spiropyran-azobenzene derivative (SPAB) can be induced to different forms in different miscellaneous solvents accompanied with different color changes and spectral characteristics at the presence of organic base DBU. In a nonpolar or low-polar solvent, SPAB exists in thermostable spiropyran form with yellow color output. While in an aprotic polar solvent, the spiropyran part isomerized to merocyanine form giving a blue color. When SPAB is subjected to a protic solvent, the alkylation reaction occurs at the oxygen generating the alkylated-SPAB with red color. This solvent-dependent property can be used for discriminating solvent type.

Key words: spiropyran; solvent; solvatochromism.

1. Introduction

Spiropyran and azobenzene are important photochromic compounds because of their potential applications in a variety of fields such as molecular machines, organic synthesis, material science and biological function modulation.[1-5] Spiropyrans are highly sensitive compounds that can be reversibly switched forth and back between colorless spiropyran (SP) and colored merocyanine (MC) form upon external stimuli such as heat, light, acid and mechanical press. [6] SP and MC forms have dramatically different polarities, charges, and molecular conformations. Typical photochromic reaction of spiropyrans is the reversible photochemical cleavage of the C-O bond in the spiropyran ring. [7] This reversible transformation has been widely used in numerous areas including self-assembly,[8] modulation of fluorescence of nanoparticles, [9-12] recognition and quantification of amino acids, [13-14] electro-optical devices, [15]molecular logic switches,[17-18] proton transfer,[19] photoswitchable biomaterials [20-21] and high-density photochemical erasable memories. [22]

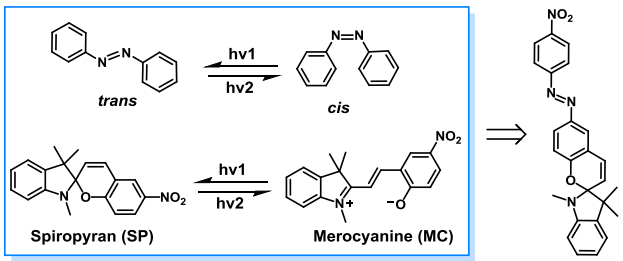

Figure 1. Photochromic transformation of spiropyrans and azobenzene and molecular design of SPAB

Spiropyran can exhibit solvatochromism behavior upon different polarity of solvents. The highly polar MC form can cause hypsochromic or bathochromic shifts depending on the solvent polarities. Therefore, spiropyrans has been developed as indicators for solvent polarity due using its negative solvatochromism .[23] Azobenzenes are widely-used dyes and photochromic molecules with a broad

application prospects in many areas.[24-27] Azobenzene dyes also find extensive applicability in analytical chemistry as acid-base, redox and metallochromic indicators. As developing novel chemosensors is highly desirable[28-31], herein, we report a colorimetric chemodosimeter which can be used to distinguish different miscellaneous solvents by blending spiropyran and azobenzene structure together. The prepared spiropyran-azobenzene (SPAB) derivative has different color responsive towards different polarity of solvents. Furthermore, as a first example, SPAB can determine the protic or aprotic property of a solvent.

2. Results and discussions

To design a probe for distinguishing different miscellaneous solvents, our idea is to make use of reversible isomerization of spiropyrans in polar solvents with the introduction of the alkali (Figure. 2). In contrast, the isomerization is difficult to occur in nonpolar solvents. Furthermore, in order to improve sensibility of spiropyran, *p*-nitro azo moiety was introduced here as electron-withdrawing moiety to enlarge the conjugation of benzopyran ring. Besides, azobenzene is also a good chromophore and indicator for pH and polarity variations. We envisioned that nucleophilic addition reaction of protic solvents (*e.g.* methanol and ethanol) with highly electrophilic indolium fragment of the MC form would occur under alkaline conditions. While for aprotic solvent, such as DMF and DMSO, such nucleophilic addition reaction cannot undergo at presence of alkaline. Therefore, discrimination of protic and aprotic solvents can be realized by using this principle.

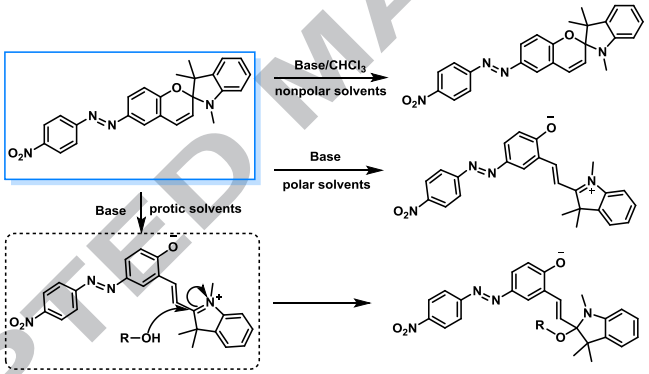

Figure 2. Principle of distinguishing different miscellaneous solvents.

The synthetic route for SPAB derivatives is depicted in **Figure 3**. Target nitro-substituted SPAB1 was prepared firstly and SPAB2 and hydroxyethyl-substituted SPAB3 were then synthesized as controls. SPAB1-**2** were prepared starting from aniline through diazotization and cyclization with intermediate **5**. The SPAB3 were synthesized through three-step reactions from 2,3,3-trimethyl-3*H*-indole **6**.

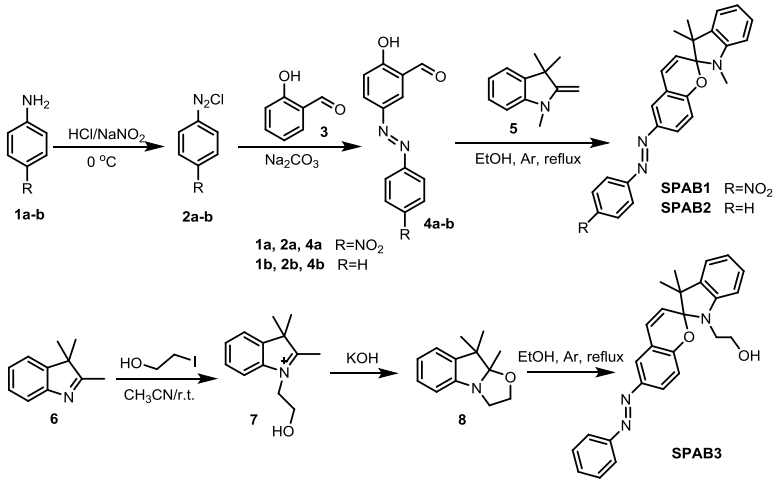

Figure 3. Synthesis routes of SPAB derivatives

After successful preparation of the SPABs, we then investigated the sensitivity and applicability of the probe towards different solvents (Figure 4A). The solution of SPAB1 in low-polar chloroform (1 mol/L) presented an orange-yellow color. When approximately equimolar amount of DBU was added to the above solution, no obvious changes on color and UV-Vis absorption spectrum can be observed even the solution stayed overnight. The results indicated that cleavage of the C-O bond of SPAB1 cannot occur in chloroform solution upon addition of DBU. While in polar solvents acetonitrile, DMF or DMSO (1 mol/L), the solution color was green, dark green and blue corresponding to the maximum UV absorption wavelengths of 590 nm, 630 nm and 635 nm, respectively. The red shift occurred with increase the polarity of the solvents. Therefore, the molecular probe can recognize acetonitrile, DMF and DMSO. The appearance of absorption bands around 600 nm was corresponding to the absorption of MC, verifying that SPAB1 turned to its open MC form. Same treatment of SPAB1 in methanol (1 mol/L) led to the color change from yellow to pale orange immediately. UV-Vis spectrum indicated the appearance of an absorption band at 540 nm. This can be explained by the fact that methanol reacted with the electrophilic indolium fragment of MC form under the catalysis of DBU. The iminium carbon atom adjacent to the positively charged nitrogen in the indolium fragment of the zwitter ionic MC species is highly electrophilic and susceptible to nucleophilic attack. When SPAB1 was subjected to protic solvent ethanol (1 mol/L), the solution color is brown with the absorption value of 500 nm. The UV-absorbing of solution in methanol occurs to red shift compared to ethanol, therefore, the molecular probes is able to distinguish methanol and ethanol.

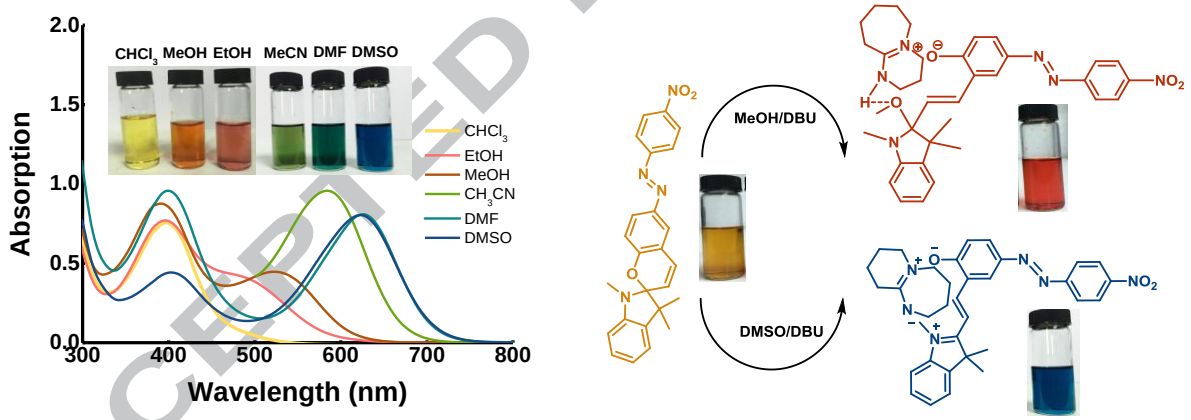

Figure 4. Color changes and UV absorption spectra of SPAB1 in different solvents containing DBU (A), principles for color changes of SPAB1-DBU system (B).

Table 1. The maximum absorption wavelength of SPAB1-DUB system in different solvents.

Solvent	λ^1_{max} (nm)	λ^2_{max} (nm)
chloroform	396	/
acetonitrile	/	583
methanol	390	525
ethanol	396	496
DMF	401	623
DMSO	399	626

In order to further identify the rationale behind this discrimination process, two control compounds SPAB2 and SPAB3 were prepared. Replacement of electron-withdrawing nitro group by hydrogen

generated SPAB2. When SPAB2 was treated by different solvents together with DBU, no obvious color or UV-Vis absorption changes were detected (Figure 5A), that is, the SPAB2 stayed in its closed form. This phenomenon confirmed that nitro substituent played a key role in stabilizing opened MC form.

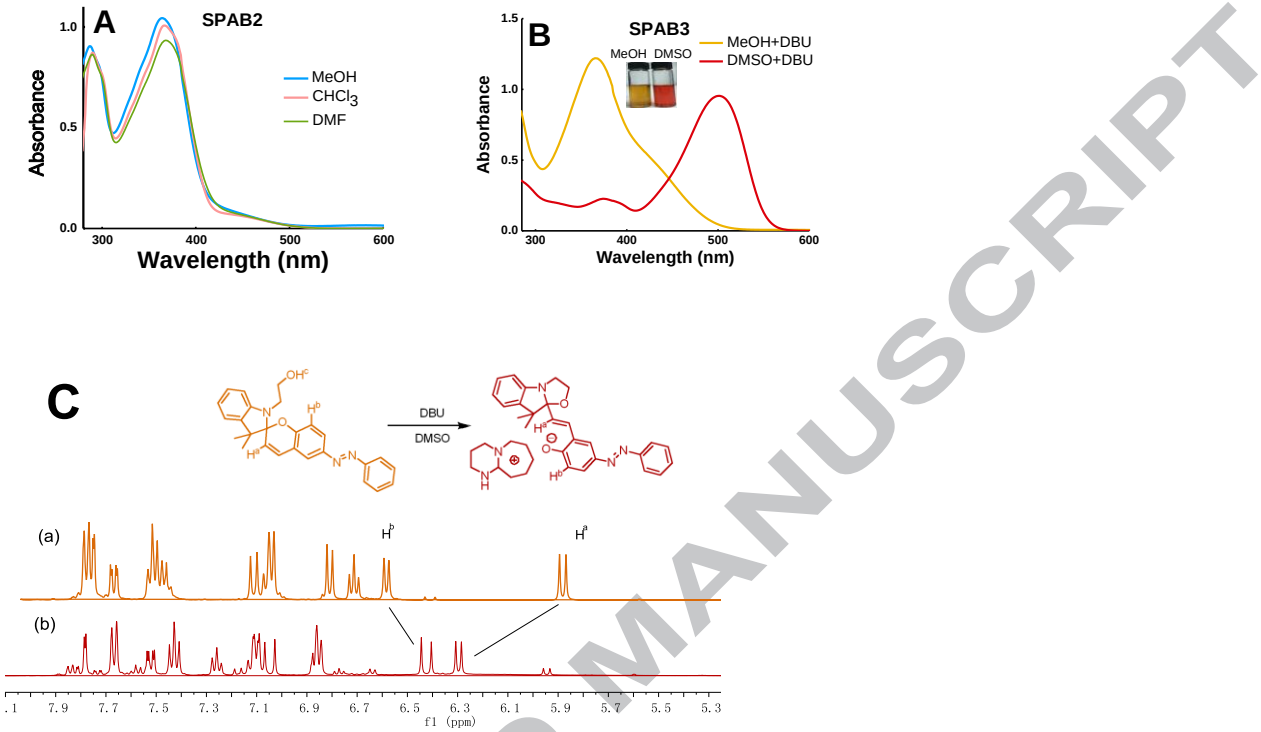

Figure 5. (A) UV absorption spectra of SPAB2 in three kinds of solvent containing DBU. (B) Color changes and UV absorption spectra of SPAB3 in methanol and DMSO containing DBU, (B) ^{1}H NMR tracking of SPAB3, (a) ^{1}H NMR spectra of SPAB3 in DMSO-d_6, (b) ^{1}H NMR spectra of SPAB3 in DMSO-d_6 after adding DBU.

Hydroxyethyl derivative SPAB3 was prepared with a view to examine the mechanism behind the color change in protic solvents. Treatment of SPAB3 with DBU in methanol caused slight color change even the solution stayed for overnight (Figure 5B). This trend is similar to that observed on SPAB2 without electron-withdrawing nitro groups, that is, the nucleophilic addition reaction of methanol with SPAB3 was difficult to proceed. Interestingly, when SPAB3 was subjected to DMSO and DBU, the color of the solution changed from orange-yellow to red. Correspondingly, the appearance of an absorption band at 513 nm was observed in UV-Vis spectrum. This is due to the intramolecular attack of hydroxyl group to iminium carbon atom adjacent to positively charged nitrogen in indolium fragment of zwitter ionic MC species catalyzed by DBU (Figure 5C). This process was further identified by ^{1}H NMR tracking of the reaction (Figure 5C). The DBU-induced absorption change is caused by the formation of new production. The signal of proton H^{c} disappears after addition of DBU because hydroxyl reacted with the spirocarbon to form a new heterocycle. The low-field shift of H^{a} is caused by deshielding effect of the olefin. The high-field change of H^{b} proton in ortho position of phenolate oxygen indicated that reaction of SPAB3 with DBU produced a spirocycle-opened species. The above observations further verified the rationale behind the color change of SPAB-DBU in methanol and ethanol.

Conclusion

Based on the solvatochromism behavior of spiropyran and azobenzene, a hybrid spiropyran-azobenzene derivative was designed and prepared as a solvent probe. Together with base

DBU, the discrimination of non-polar solvent, aprotic polar solvent and protic polar solvent was achieved using the designed SPAB. Different types of solvents present different color output towards SPAB-DBU system and the rationale behind this was also investigated. The results described here can be used as an auxiliary method for fast detection of solvent types

Experimental

Chemicals and instrumentations

Melting points (mp) were recorded on Büchi B540 apparatus (Büchi Labortechnik AG, Flawil, Switzerland) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM-400 (400 MHz) spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. Chemical shifts are reported in δ (parts per million) values. Electrospray ionization (ESI) mass spectrometry was performed in a HP 1100 LC-MS spectrometer. Analytical thin layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized with ultraviolet (UV) light. Column chromatography was performed using silica gel (Hailang, Qingdao) 200-300 mesh. Unless otherwise noted, reagents and solvents were used as received from commercial suppliers. Yields were not optimized. All reactions were carried out under a protective atmosphere of drying nitrogen or utilizing a calcium chloride tube.

Synthesis the target compounds

Synthesis of 2-hydroxy-5-((4-nitrophenyl)diazenyl)benzaldehyde (**4a**). To a solution of 4-nitroaniline **1a** (0.05 mol) in distilled water (100 mL), 50 mL of 3 M hydrochloride was added dropwisely under the condition of ice bath. Then 3.6 M sodium nitrite aqueous solution was added to the above solution slowly. The mixture was kept on vigorously stirring for 1 h. After that a mixture of salicylic aldehyde 25 mL (0.05 mol) and 1.1 M sodium carbonate aqueous solution were added into the reaction mixture. The reaction stirred for 4 h at room temperature and neutralized with hydrochloride aqueous solution. The precipitate was washed with water and dried. Recrystallization of the crude product with ethanol gave **4a**. Yield, 64%; Melting point, 196.5-197.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ11.96 (s, 1H), 10.38 (s, 1H), 8.41 (d, J = 8.7 Hz, 2H), 8.23 (s, 1H), 8.18-8.09 (m, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.32-7.18 (m, 1H); ^{13}C NMR(101 MHz, DMSO-d_6) δ 160.1, 135.9, 134.1, 130.3, 129.4, 128.6, 121.54,120.2, 117.7, 112.2, 111.0.

Synthesis of 2-hydroxy-5-(phenyldiazenyl)benzaldehyde (**4b**). The **4b** was synthesized according to a similar procedure for preparing **4a**. Yield, 67%; Melting point, 128.1-129.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.55 (s, 1H), 10.39 (s, 1H), 8.20 (s, 1H), 8.11 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 7.3 Hz, 2H), 7.57 (m, 3H), 7.21 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.52, 163.39, 151.82, 144.7, 131.1, 129.7, 129.4, 123.7, 122.6, 122.3, 118.4.

Synthesis of 9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (**8**). A solution of 2,3,3-trimethyl-3H-indole (12.56 mmol) and 2-iodoethyl alcohol (12.56 mmol) in acetonitrile (30 mL) was refluxed for 24 h under nitrogen protection. After cooling down to room temperature, the solvent was removed under reduced pressure. The residue was suspended in hexane (30 mL) and the mixture was filtered. The resulting solid was recrystallized from chloroform (40 mL) to afford 1-(2-hydroxyethyl-2,3,3-trimethyl-3H-indolium iodine (**7**). A solution of **7** (4.89 mmol) and KOH (7.83 mmol) in water (15 mL) was stirred at 25 °C for 20 min, and then was extracted with diethyl ether (3 × 30 mL). The organic phase was concentrated under reduced pressure to afford **8**. Yield, 67%; Melting point, 44.3-45.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19-7.08 (m, 2H), 6.98-6.92 (m, 1H), 6.78 (d, 1H, J = 6.6 Hz), 3.90-3.49 (m, 4H), 1.47 (s, 3H), 1.42 (s, 3H), 1.21 (s, 3H); ^{13}CNMR ($CDCl_3$, 101MHz) δ 150.6, 140.0, 127.5, 122.4, 121.7, 112.0, 109.0, 63.0, 50.1, 47.0, 28.1, 20.8, 17.6.

Synthesis of 1',3',3'-trimethyl-6-((4-nitrophenyl)dizenyl)spiro[chromene-2,2'-indo-line] (**SPAB1**). **4a** (1.0 mmol) was dissolved in 10 mL ethanol. The mixture was heated to reflux for 30 min. Then fisher base **5** (1.0 mmol) was added into mixture drop wise. The reaction was held under Argon atmosphere for 12 h. After completion of the reaction, the mixture was cooled down to room temperature. The crude product was obtained by filtering and

washed with ethanol. Recrystallization by ethanol afforded the final product as yellow solid. Yield, 44%; Melting point, 209.8-210.6 °C; ^{1}HNMR (400 MHz, DMSO-d_6) δ 1.13 (s, 3H), 1.25 (s, 3H), 2.70 (s 3H), 5.94 (d, J = 10.28 Hz, 1H), 6.60 (d, J = 8.28 Hz, 1H), 6.79 (t, J = 7.52 Hz, 1H), 6.92 (d, J = 8.72 Hz, 1H), 7.12 (m, 2H), 7.22 (d, J = 10.28 Hz, 1H), 7.78 (dd, J = 8.68 Hz, 2.44 Hz, 1H), 7.87 (d, J = 2.4 Hz, 1H), 7.94 (d, J = 8.72 Hz, 2H), 8.04 (d, J = 8.68 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.5, 158.1, 152.9, 147.5, 135. 8, 128.8, 127.6, 126.3, 124.9, 123.2, 121.6, 120.7, 119.1, 115.6, 109.7, 106.8, 105.5, 86.3, 51.5, 28.6, 25.7, 19.8; HRMS (ESI), m/z $[M+H]^+$ calcd for $C_{25}H_{25}N_4O_3^+$, 427.1770; found, 427.1771.

Synthesis of 1',3',3'-trimethyl-6-(phenyldiazenyl)spiro[benzofuran-2,2'-indole] (**SPAB2**). **4a** (1.0 mmol) was dissolved in 10 mL ethanol. The mixture was heated to reflux for 30 min. Then fisher base **5** (1.0 mmol) was added into mixture drop wise. The reaction was held under Argon atmosphere for 12 h. After completion of the reaction, the mixture was cooled down to room temperature. The crude product was obtained by filtering and washed with ethanol. Recrystallization by ethanol afforded the final product as yellow solid. Yield, 56%; Melting point, 166.4-166.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86-7.79 (m, 3H), 7.74 (d, J = 8.6 Hz, 1H), 7.55 (dt, J = 21.6, 7.1 Hz, 3H), 7.21 (d, J = 10.3 Hz, 1H), 7.15-7.07 (m, 2H), 6.88 (d, J = 8.6 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 5.91 (d, J = 10.3 Hz, 1H), 2.70 (s, 3H), 1.25 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.9, 151.9, 147.5, 145.9, 136.1, 130.8, 129.4, 129.0, 127.5, 125.4, 122.2, 121.4, 120.9, 120.5, 119.1, 115.3, 106.9, 105.0, 51.6, 28.5, 25.4, 19.7. HRMS (ESI), m/z $[M+H]^+$ calcd for $C_{25}H_{24}N_3O^+$, 382.470; found. 382.472.

Synthesis of 2-[3',3'-dimethyl-6-(phenyldiazenyl)spiro[benzofuran-2,2'-indole]-1'-yl)ethan-1-ol (**SPAB3**). The mixture of 9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (**8**) (2.0 mmol) and **4b** (2.0 mmol) was dissolved in ethanol (20 mL). Then the reaction was refluxed under argon overnight. After completion of the reaction, half of the solvent was removed in vacuum, cooled and filtered to give the crude product. Further purification by column chromatography (petroleum ether/ethyl acetate = 10: 1) afforded the target product as reddish brown solid. Yield, 47%; Melting point, 194.3-195.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.4 Hz, 2H), 7.76 (dd, J = 8.6, 2.3 Hz, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.25 (s, 1H), 7.18 (dd, J = 8.0, 7.3 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.94 (d, J = 10.3 Hz, 1H), 6.88 (dd, J = 12.8, 5.5 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 5.73 (d, J = 10.3 Hz, 1H), 3.88-3.69 (m, 2H), 3.60-3.45 (m, 1H), 3.34 (ddd, J = 15.5, 10.3, 5.6 Hz, 1H), 1.32 (s, 3H), 1.18(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 152.7, 147.3, 146.8, 136.2, 130.4, 129.4 129.0, 127.7, 125.9, 122.5, 121.9, 121.00, 120.6, 119.6, 118.8, 115.6, 106.8, 105.6, 60.9, 52.5, 46.1, 25.9, 20.2. HRMS (ESI), m/z $[M+Na]^+$ calcd for $C_{26}H_{25}N_3O_2Na^+$, 412.203; found, 412.226.

Characterization.

UV–vis absorption spectroscopy was used to detect the change of absorption profiles of target compounds. Absorption spectra were recorded on a Lambda 25 UV/vis spectrometer (PerkinElmer, Shanghai). Target compounds were dissolved in different solvents using a microcuvette and subjected to the test. The changes of the SPAB3 before and after adding DBU was investigated in detail by ^{1}H NMR spectroscopy.

Acknowledgments

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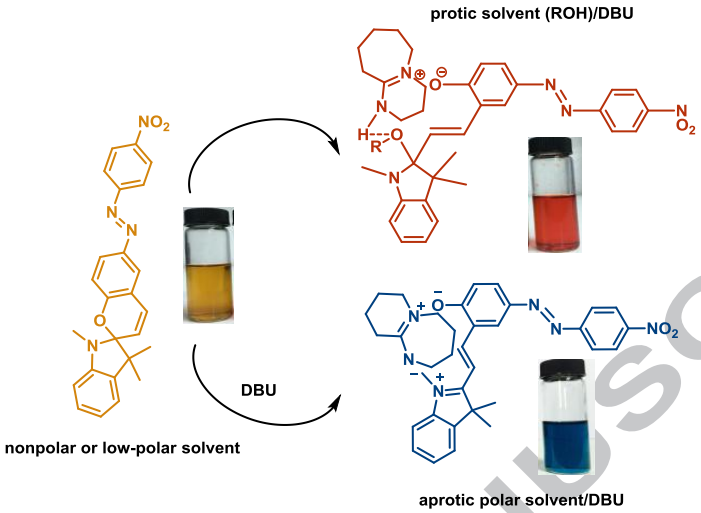
References

1. Feringa BL, van Delden RA, Koumura N, Geertsema EM. *Chem Rev*. 2000; 100: 1789.
2. Herder M, Schmidt BM, Grubert L, Pätzel M, Schwarz J, Hecht S. *J Am Chem Soc.* 2015; 137: 2738.
3. Zhou JW, Guo X, Katz HE, Bragg AE. *J Am Chem Soc.* 2015; 137: 10841.
4. Guo X; Zhou JW; Siegler MA; Bragg AE; Katz HE. *Angew Chem Int Ed.* 2015; 54: 4782.
5. Fredrich S, Bonasera A, Valderrey V, Hecht S. *J Am Chem Soc.* 2018; 140: 6432.
6. Minkin VI. *Chem Rev*. 2004; 104: 2751.
7. Keum SR, R SJ, Ahn SM, Lim SS, Kim SH, Koh K. *Dyes Pig*. 2007; 74: 343.
8. Descalzo AB, Jiménez D, Haskouri JE. *Chem Com*. 200; 38: 562.
9. Kim TH, Swager TM. *Angew Chem Int Edit*. 2003; 42: 4803.
10. Wojtyk JT, Kazmaier PM, Buncel E. *Chem Mater*. 2001;13: 2547.
11. Chen J, Zeng F, Wu S, Su J, Tong Z. *Small*. 2009; 5: 970.
12. Cui H, Liu H, Chen S, Wang R. *Dyes Pigm*. 2015;115: 50.
13. Manuel S, Kraeling K, Richter K, Xie XL, Steuber H, Meggers E. *Angew Chem Int Edit*. 2014; 53: 305.
14. Liu YY, Fan MG, Zhang SX. *New J Chem.* 2007; 31:1878.
15. Wang LF, Chen JW, Chen JW. *Mater Chem Phys*. 2012;136: 151.
16. Berkovic G, Krongauz V,Weiss V. *Chem Rev*. 2000; 100: 1741.
17. Jordan P, Fromme P, Witt HT, Klukas O, Seanger W, Krauss N. *Nature*. 2001; 411: 909.
18. Mancois F, Pozzo JL, Pan J, Adamietz F, Rodriguez V, Ducasse L, Castet F, Plaquet A, Champagne B. *Chem Eur J*. 2009;15: 2560.
19. Raymo FM, Alvarado RJ, Giordani S, Cejas MA. *J Am Chem Soc*. 2003; 125: 2361.
20. Zhu LY, Wu WW, Zhu MQ, Han JJ, Hurst JK, Li ADQ. *J Am Chem Soc*. 2007; 129: 3524.
21. Zhu MQ, Zhang GF, Li C, Aldred MP, Chang E, Drezek RA, Li ADQ. *J Am Chem Soc.* 2011; 33:365.
22. Hirshberg Y. *J Am Chem Soc.* 1956; 78: 2304.
23. Zacharias P, Gather MC, Koehnen A, Rehmann N, Meerholz K. *Angew Chem Int Edit*. 2009; 48: 4038.
24. Parker RM, Gates JC, Rogers HL, Simth PGR, Grossel MC. *J Mater Chem*. 2010; 20: 9118.
25. Puntoriero F, Ceroni P, Balzani V, Bergamini G, Vögtle F. *J Am Chem Soc*. 2007; 129: 10714.
26. Kim Y, Phillips JA, Liu HP, Kang HZ, Tan WH. *PNAS*, 2009;106: 6489.
27. Wang J, Liu HB, Ha CS. *Tetrahedron*. 2009; 65:9686.
28. Wang HM, Liu J, Han AT, Xiao NN, Xue ZS, Wang G, Long JF, Kong DL, Liu B, Yang ZM, Ding D. *ACS Nano*, 2014; 8: 1475.
29. Zheng XJ, Zhu WC, Liu D, Ai H, Huang Y, Lu ZY. *ACS Appl Mater Interfaces*, 2014; 6: 7996.
30. Fang MX, Adhikari R, Bi JH, Mazi W, Dorh N, Wang JB, Conner N, Ainsley J, Karabencheva-Christova TG, Luo FT, Tiwari A, Liu HY. *J. Mater Chem B,* 2017; 5: 9579.
31. Guo ZQ, Shin I, Yoon J. *Chem Commun.* 2012; 48: 5956.

Highlights:

1. Photochromic spiropyran and azobenzene were linked together by covalent bond.
2. Spiropyran-azobenzene can be induced to different forms in different solvents.
3. Different spiropyran-azobenzene form gave different color output as a solvent indicator.

Graphical Abstract:



32.