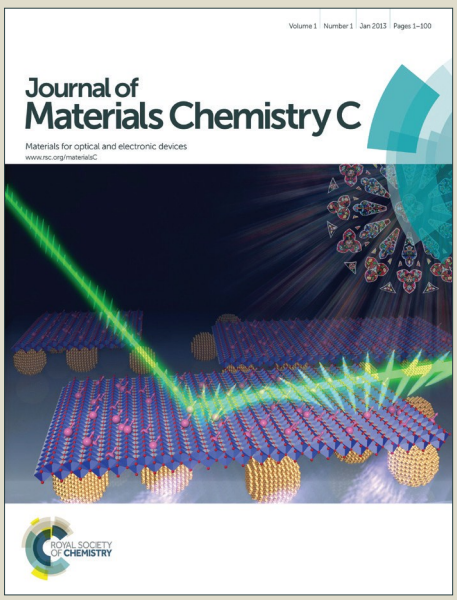
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Methyl ketone bridged molecule as multi-stimuli-responsive color switch for electrochromic device

Yu-Mo Zhang,*[b] Fuli Xie,[a] Wen Li,[a] Yuyang Wang,[a] Weiran Zhang,[a] Xiaojun Wang,[a] Minjie Li,[a] and Sean Xiao-An Zhang*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A new multi-stimuli-responsive **M5** with methyl ketone bridge has been developed to fabricate visible-near infrared absorbing electrochromic device. The basochromic and electrochromic properties of methyl ketone **M5** with nitronaphthalene was studied in detail by spectroelectrochemical method and Density Functional Theory (DFT) calculation. The colorless **M5** can be switched to green-yellow with broad visible-near infrared absorption (400-500 nm, 550 -800 nm), stimulated by base and electricity. And multi electron transfer- proton transfer mechanism (electrobase) of electrochromism for **M5** has been proved by cyclic voltammetry (CV) and in-situ UV-Vis spectroscopy. This multi-stimuli color switch has been successfully applied in electrochromic device with attractive properties such as short switching time and good reversibility.

1. Introduction

Multi-responsive molecular switches,[1] which can be switched by external multi-stimulus, such as light,[2] electricity,[3] heating,[4] acid/base,[5] have emerged as an important area of color switch, due to that it can be applied in multi-functional display,[6] intelligent disguise,[7] multi-purpose sensor,[8] complex logic-gate operation[9] and multimode data storage.[10] However, a limited number of multi-stimuli-responsive color switches of a single smart molecule has been reported.[11]

To develop new kinds of multi-responsive color switches, the strategy of combining/integrating the known switch units with conjugate linkers[12] and non-conjugation spacers[13] has been used widely. But there are many disadvantages for this method, such as complicated synthesis procedure, required precise molecular band gaps matching, degraded excellent photophysical properties. Another strategy of developing multi-responsive color switches is to use multi-responsive switch units, such as azoic,[14] dithienylethenes,[15] and spiropyrane,[16] which responds to two or more different stimulus. The key of this strategy is to develop a new multi-responsive switch unit for multi-responsive color switches. In our group, we have reported that pH-responsive methyl ketone can be used as electro-switching unit for molecular color switches.[17] Thus, we focus attention on methyl ketone unit, which enables a reversible enol–ketone tautomerization by acid/base and electrical (electroacid/base). And this new multifunctional unit displays outstanding photochemical properties, such as the color tunability, the high molar absorption coefficient by varying substituents on aromatic rings.

In order to expand the application of methyl ketone unit, we should exploit new photoelectric properties, such as near infrared absorption for infrared camouflage materials. Thus, we synthesized the new methyl ketone bridged color switch **M5** with nitronaphthalene which exhibits yellow-green with broad visible-near infrared absorption (400-500 nm, 550 -800 nm), stimulated by base and electricity. The electrochromic and basochromic properties of **M5** have been studied in detail by spectroelectrochemical method and density functional theory. Our multi-responsive color switch has been applied in electrochromic device with several appealing properties, such as short switching time and good reversiblity.

2. Experimental

2.1 Materials

1,5-dinitronaphthalene, $Pd[PPh_3]_2Cl_2$, Trimethyl silyl acetylene (TMSA), potassium tert-butoxide, Tetrabutylammonium fluoride (TBAF), and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were of analytical grade and purchased from Aladdin. N-dimethylformamide (DMF) was distilled from calcium hydride under nitrogen.

2.2 Characterizations

Shimadzu UV-2550 PC spectrophotometer was used to record UV-Vis absorption spectra. *in-situ* UV-Vis spectroscopy were measured by combining Bio-logic electrochemical work station with Shimadzu UV-2550 PC spectrophotometer. The Cyclic

*a. State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, Jilin 130012, China. *E-mail: seanzhang@jlu.edu.cn.*
*b. College of Chemistry, Jilin University, Changchun, Jilin 130012, China. *E-mail: zhangyumo@jlu.edu.cn. Fax: +86-431-85163812; Tel: +86-431-85163810*
† Electronic supplementary information (ESI) available. See DOI:10.xxx/x0xx00000x

voltammograms were measured by Bio-logic electrochemical work station using the three-electrode cell, which consisted of a glass-carbon working electrode (Shenhua, China), an $AgNO_3$/Ag reference electrode (Shenhua, China) and a Pt-wire counter electrode (Shenhua, China). ESI-HRMS analysis were recorded with Agilent 1290-micrOTOF-Q II mass spectrometer. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were measured on Varian Mercury (300 MHz).

2.3 Calculation

M5 and **M5-enolate** were fully optimized using the Gaussian 09 program by B3LYP/6-31+g(d,p).[18] In order to ensure the two structures corresponding to true minima of the potential energy surface, the same level of theory B3LYP/6-31+g(d,p) was used to calculate the vibrational spectrum.

2.4 Electrochromic device

1.0×10^{-2} M **M5** in DMF solution containing 0.1 M $TBAPF_6$ was injected into sandwich-type ITO cells, which was constructed with two ITO as electrodes and Polydimethylsiloxane as the spacer.

2.5 Synthesis

1-iodo-4-methoxybenzene: Under nitrogen atmosphere, 5 mmol iodine and 2 mmol periodic acid were added to 2 ml anisole. Then the reaction was stirred for 3 h at 60 ^{o}C. After the reaction was complete by TLC analysis, CH_2Cl_2 (20 ml) was added and the reaction mixture was washed with sodium hyposulfite aqueous solution and water (3 times), the organic layer was dried and concentrated under reduced pressure. The crude residue was recrystallized to yield yellow solid (1.2 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.56 (d, *J* = 9.1 Hz, 2H), 6.68 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ =59.48, 138.21, 116.38, 82.69, 55.32. m.p.: 43.5-44.4 °C.

5-nitronaphthalen-1-amine: 1,5-dinitronaphthalene (1 g, 5 mmol) was dissolved in a mixture of water (10 ml) and ethanol (10 ml) at 65 ^{o}C. Then, $Na_2S\bullet9H_2O$ (0.95 g, 4 mmol) was added in 3 portions. The mixture was monitored by TLC and the precipitate was collected by filtration and washed with water. After the solvent was removed, the residual solid was purified by flash chromatography(hexane/ethyl acetate=8:1) to afford a brown-red solid (0.63 g, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.13 (d, J = 7.1 Hz, 2H), 7.90 (d, J = 8.5 Hz, 1H), 7.49 (ddd, J = 8.1, 6.9, 2.9 Hz, 2H), 6.90 (d, J = 6.6 Hz, 1H), 4.25 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ = 147.11, 146.41, 131.10, 129.31, 125.83, 123.84, 123.81, 122.31, 109.24, 108.91. LC-HRMS: calcd for $C_{10}H_9N_2O_2$ 189.0659, found 189.0668. m.p.: 160.3-161.1 °C.

1-iodo-5-nitronaphthalene: The solution of 5-nitronaphthalen-1-amine (1.13 g, 6 mmol) in 13 ml acetic acid was dropped to the mixture solution of $NaNO_2$ (480 mg) and concentrated sulfuric acid (5 mL) at 0 ^{o}C and stirred for 0.5 h. Then, the mixture solution was poured into urea (0.1 g), ice (8 g), KI (18 g), and water (18 ml) and stirred for 8 h. The precipitate was collected by filtration and washed with CH_2Cl_2. After the solvent was removed and the residual solid was purified by flash chromatography (hexane/ethyl acetate=9/1) to afford pale-yellow solid (1.75 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.48 (d, *J* = 8.8 Hz, 2H), 8.28 – 8.17 (m, 2H), 7.64 (dd, *J* = 8.4, 7.6 Hz, 1H), 7.39 (dd, *J* = 8.6, 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ =147.17, 139.26, 138.53, 134.73, 129.92, 125.77, 125.73, 124.18, 123.75, 99.75. m.p.: 116.7-117.8 °C.

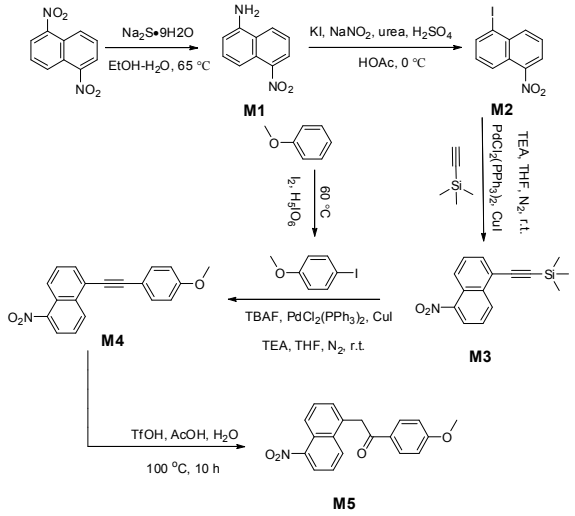
Trimethyl((5-nitronaphthalen-1-yl)ethynyl)silane: To a stirred solution of 1-iodo-5-nitronaphthalene (7, 0.3 g), $Pd[PPh_3]_2Cl_2$ (15 mg), CuI (10 mg), THF 2ml and Et_3N 2 ml was added TMSA by syringe under nitrogen atmosphere. The mixture was stirred at room temperature over night. The residue was washed with sat. NH_4Cl (aq.) and H_2O, the organic layer was dried and concentrated under reduced pressure. The crude residue was recrystallized from EtOH to yield the yellow solid (0.25 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.70 (d, *J* = 8.4 Hz, 1H), 8.50 (t, *J* = 8.6 Hz, 1H), 8.24 (t, *J* = 6.8 Hz, 1H), 7.83 (d, *J* = 7.1 Hz, 1H), 7.70 – 7.58 (m, 2H), 0.40 – 0.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 134.19, 132.79, 132.05, 128.56, 125.01, 124.97, 124.30, 123.68, 121.86, 120.00, 101.80, 101.50, -0.04. LC-HRMS: m/z calc. for $C_{25}H_{28}NSi$ 370.1986, found 370.1980. m.p.: 89.5-90.7 °C.

1-((4-methoxyphenyl)ethynyl)-5-nitronaphthalene: To a stirred solution of trimethyl((5-nitronaphthalen-1-yl)ethynyl)silane (0.27 g, 1 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg) and CuI (20 mg) in THF (10 mL) and Et_3N (10 mL), TBAF solution (1M in THF, 2.5 ml) was added slowly at room temperature. After the reaction was stirred for 1h, 1-iodo-4-methoxybenzene (0.28 g, 1.2 mmol) was then added in and the reaction solution was stirred over night. The solvents of the reaction mixture was distilled off after the reaction, and the residue was extracted with ethyl acetate, and washed with sat. NH_4Cl (aq.) and H_2O. Then separated off the aqueous phase, and the organic phase was dried over $MgSO_4$. After evaporation of the solvent, and the crude product was purified by column chromatography to afford a pale yellow solid (0.27 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.80 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 8.26 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.74 – 7.62 (m, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 160.16, 147.06, 134.03, 133.23, 132.86, 131.27, 128.73, 125.17, 124.77, 124.29, 123.04, 122.43, 114.79, 114.23, 95.99, 85.26, 55.38. m.p.: 107.0-108.0 °C.

1-(4-methoxyphenyl)-2-(5-nitronaphthalen-1-yl)ethanone: 1-((4-methoxyphenyl)ethynyl)-5-nitronaphthalene (50 mg, 0.165 mmol) was added to the mixture solution of 40 ul water, 50 ul TfOH and 5 ml acetic acid at 100 ^{o}C, and then stirred for 10 h. The reaction mixture was then added to water and extracted with ethyl acetate. The combined organic layers were dried over MgSO4, filtered, and evaporated in vacuo. The residue was purified by flash column chromatography to afford the yellow solid (26 mg, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ= 8.43 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 7.7 Hz, 2H), 8.07 (d, J = 8.9 Hz, 2H), 7.66 (dd, J = 8.7, 7.1 Hz, 1H), 7.59 – 7.45 (m, 2H), 6.98 (d, J = 8.9 Hz, 2H), 4.75 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ =195.18, 163.94, 147.73, 133.47, 132.64, 130.77, 130.29, 129.68, 129.44, 128.78, 125.64, 124.39, 123.22, 122.54, 114.03, 55.54, 43.24. LC-HRMS: calcd for $C_{19}H_{16}NO_4$ 322.1079, found 322.1070. m.p.: 119.0-119.9 °C.

3. Results and discussion

3.1 Sythesis of the Methyl Ketone Bridged Molecule



Scheme 1. The synthetic route of **M5**.

For methyl ketone bridged molecules, the simple and common synthesis methods are the Friedel–Crafts acylation[19] and the alkyne hydrolysis reaction.[20] Due to the limitation of naphthylacetic acid synthetic method, the alkyne hydrolysis method was chosed to synthesis **M5**. And the synthetic route used to prepare the compound of **M5** is shown in Scheme 1. First, **M1** was obtained from 1,5-dinitronaphthalene by selective reduction, which was then diazotized under acidic conditions to 1-iodo-5-nitronaphthalene (**M2**). Then, **M4** was prepared by a modified one-pot process of the sonogashira coupling[21] of 1-iodo-4-methoxybenzene with **M3**, which was obtained by the sonogashira coupling of **M2** with TMSA. Finally, the methyl ketone molecule **M5** was obtained by hydrolyzed under acidic condition at 100 °C. All of the compounds used in this paper were purified and fully characterized by conventional analytical methods, such as ^{1}H-NMR, ^{13}C-NMR, MS etc.

3.2 Basochromic property of the Methyl Ketone Bridged Molecule

As shown in Figure 1, two new absorption bands at 550 -800 nm (λ_{max} = 692 nm) and 400-500 nm (λ_{max} = 432 nm) range are observed by adding base in DMF solution of **M5**, and the color of **M5** changed from colorless to green-yellow. This result suggests that the methyl ketone moiety of **M5** is isomerized to enolate. And the ketone-enolate isomerization is proved by NMR spectra, as shown in Figure S1-S3. The change in absorption bands of **M5** is in proportional to the base strength and concentration (Figure 1B). The enolate of **M5** (**M5-enolate**) can be reverted to its original methyl ketone structure **M5** by addition acid. As shown in Figure 1A, acid leads to a decrease in 692 nm and 432 nm absorption bands. This indicates that **M5** can be isomerized reversibly upon alternant stimulations with base and acid. And the ketone-enolate isomerization of **M5** can be switched by the strong base (NaOH, Lithium bis(trimethylsilyl)amide) and most of acid (HCl, CF_3COOH and HCOOH) in aprotic solvent (DMSO, CH_3CN), as shown in Figure S4-S8. To further investigate the stability and reversibility of this switch, **M5** is treated repetitively for three times with alternant additions of base and acid monitoring at 432 nm under an inert environment. Fortunately, no distinct degradation was observed. Thus, the color switch **M5** is stable under an inert environment.

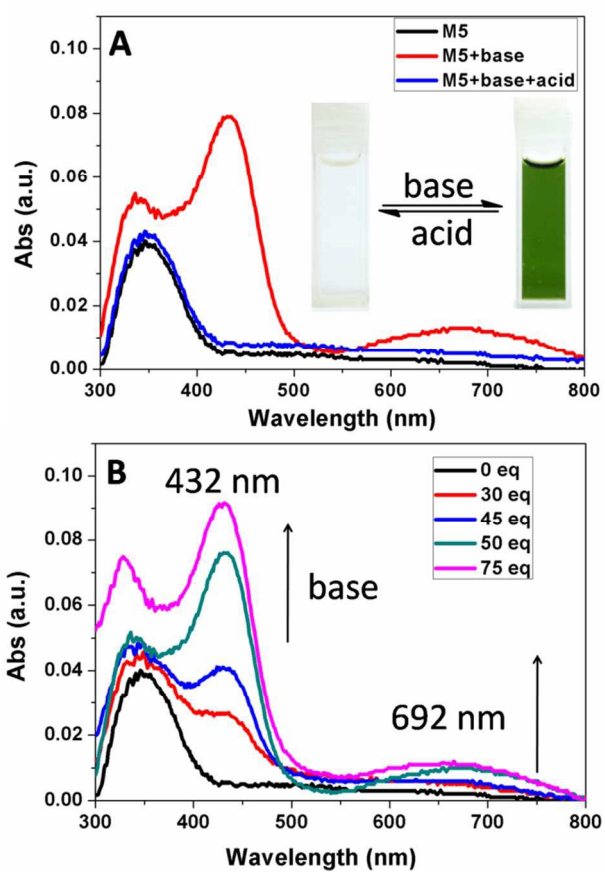


Figure 1. (A) Absorption spectra of **M5** (1.0×10^{-5} M, black curve), treated with potassium tert-butoxide (red curve), then neutralized with CH_3COOH (blue curve) in DMF. (B) Absorption spectra of **M5** (1.0×10^{-5} M) in the presence of potassium tert-butoxide (0eq, 30eq, 45eq, 50eq and 75eq) in DMF.

To further understand the basochromic properties of **M5**, the relationship of their structure and the absorption bands was provided by density functional theory. As shown in Figure 2, the absorption band for **M5-enolate** at 692 nm is assigned to the intramolecular charge transfer bands from HOMO, which is mainly localized on its oxygen anion portion, to LUMO, which is mostly localized on the nitro group. And the absorption band at 432 nm is assigned to the π-π* transition from HOMO to LUMO+2, which is distributed over the conjugated system.

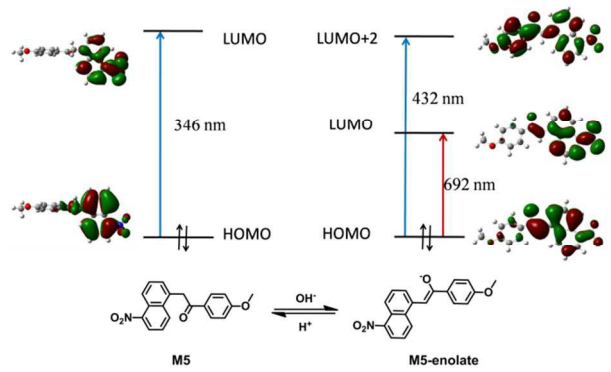


Figure 2. The HOMO (bottom) and LUMO or LUMO+2 (top) orbits of **M5**, and **M5-enolate**.

3.3 Electrochromic property of the Methyl Ketone Bridged Molecule

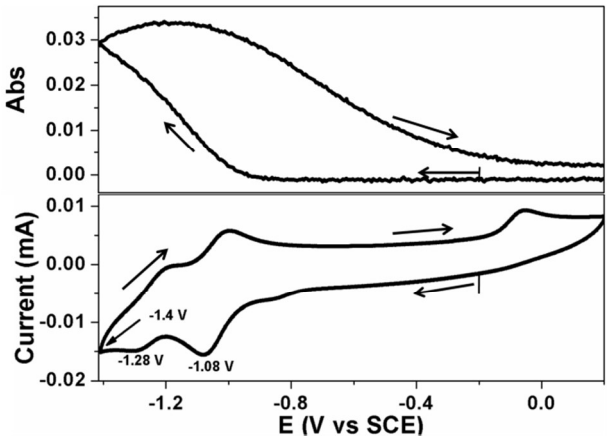


Figure 3. Changes in the absorption at 432 nm (top) and the cyclic voltammogram (bottom) of **M5** (1.0×10^{-3} M) in DMF with 0.1 M $TBAPF_6$ using a glassy carbon electrode (d = 3 mm). Scan rate: 50 mV s^{-1}.

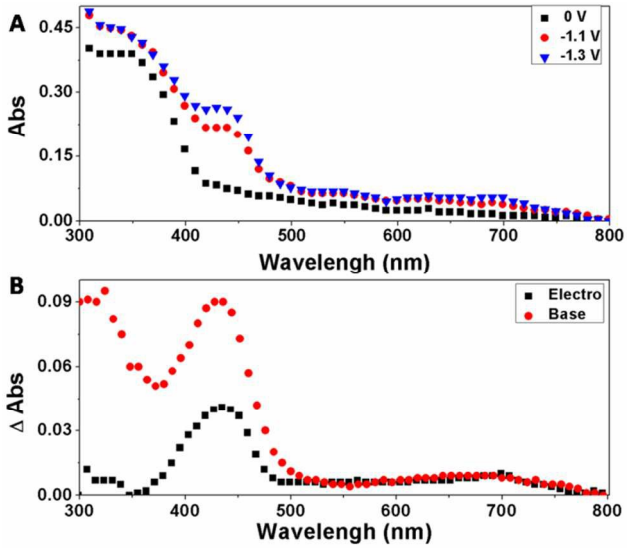


Figure 4. (A) Absorption spectra of **M5** in DMF with 0.1 M $TBAPF_6$ at 0 V (black), -1.1 V (red) and -1.3 V (blue) about 60 s. (B) Differential absorption spectra of **M5** in DMF after stimulated by -1.3 V(black) or base (red).

The photoelectrochemical property of **M5** was first studied by electrochemical work station combined with *in situ* UV-vis spectrometers (Figure S9) in DMF solution. As shown in Figure 4A, two absorption bands at 695 nm and 432 nm appeared at -1.1 V corresponding to the first reductive peak of **M5** (Figure 3), and the color of **M5** solution changed from colorless to green-yellow. The intensity of 695 nm and 432 nm futher increased at higher voltage -1.3 V corresponding to the second peak of **M5**. This phenomenon confirms that the color of **M5** can be switched by electrical method. More interestingly, the absorption peak (695 nm, 432 nm) of **M5** stimulated by electric field is identical to the absorption peak (692 nm, 432 nm) of **M5-enolate** generated by addition base, as shown in Figure 4B. Thus, we believe that the electrically generated colored intermediate is **M5-enolate**. This unique phenomenon of methyl ketone molecules is consistent with our previous research.[17] However, there are unobvious difference between the absorption spectra stimulated by -1.3 V or base in Figure 4B. This finding indicates that the photochemical property of the **M5-enolate** can be tuned by the microenvironment effect, such as electrolyte, polarity and other unknown factors. In additon, the electrochemical intermediate of **M5** is other important factor for the unobvious difference.

To fully understand the mechanism of this electrochemical colour switching, the assignment of the reductive peak is important experiment. Compared with nitrobenzene (-1.20 V and -1.92 V) and 1,2-diphenylethanone (-2.0 V), the first reductive peak of **M5** at -1.1 V can be affiliated with the first reduction of nitro group, the second reductive peak at -1.2 V is assigned to the reduction of carbonyl, and the third reductive peak at -1.8 V (Figure S10) is the second reductive peak of nitro group. To further understand the relationship of the change absorbance and the redox property, cyclic voltammetry (CV) of **M5** was monitoring by *in situ* UV-vis spectrometers in DMF. As shown in Figure 3, the intensity of 695 nm is dependent on the redox state of **M5**. The intensity of 695 nm (green-yellow) began to increase when the first reductive peak of **M5** was observed at -1.1 V; further increased after the second reductive peak at -1.28 V and the starting voltage of the third reductive peak at -1.4 V; then decreased right after the oxidative peak of the second reductive peak at -1.19 V; and finally vanished (Figure 3).

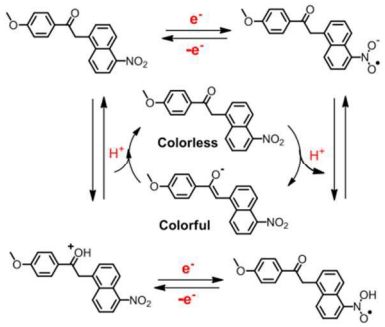


Figure 5. The electrochromic mechanism of **M5** with one-electron reduction mechanism.

Based on the data of the in situ electrochemical spectra, the intermediate **M5-enolate** is generated by the proton transfer from the methylene of **M5** to the reductive product of **M5**, such as radical anion of nitro, radical anion of carbonyl, the dianion of nitro. Thus, the electrochromic mechanism of **M5** is proton coupled electron transfer, as shown in Figure 5 (one-electron reduction mechanism) and Figure S11 (three-electron reduction mechanism). In this diagram, radical anion/dianion of nitro or carbonyl can induce the proton transfer of methylene, similar to chemical base. Thus, the radical anion/dianion is named

electrobase, and the mechanism of proton transfer is defined as electrobase mechanism.

To verify the switching reversibility of the electrochromic property of **M5** in a more practical device, we fabricated the thin-liquid film ITO devices. As shown in Figure 6A, the new absorption bands at 695 nm and 432 nm was appeared in the ITO device of **M5,** and the color of the device changed form colorless to green-yellow when a bias voltage of -3.0 V was applied. In addition, the color change and absorbance at 695 nm and 432 nm of **M5** device can vanish reversibly at +1.0 V. Thus, these results demonstrate that **M5** can be used as electrochromic material.

Then, the electrochromic performance of **M5** was evaluated by response time, the stability and the coloration efficiency. As shown in Figure 6B, the intensity of absorbance of **M5** device depends on the switching time. The high absorbance in ITO device can be achieved with the relatively long switching time, and the low absorbance can be achieved with the short switching time. The detectable absorbance change of ITO device can be obtained by -3.0 V for 10 ms. The coloration efficiency of **M5** device is approximately 80 $cm^2 \bullet C^{-1}$, as shown in Figure 6C and supporting infromation. To investigate the stablility of **M5** device, the absorbance change at 432 nm of the thin film device was monitored by absorption spectroscopy in situ (Figure 6D). The absorbance of the cell was perfectly maintained with no sign of degradation after 17 test cycles. The encouraging result obtained hereon demonstrates that the electrochromic performance of **M5** is fully reversible.

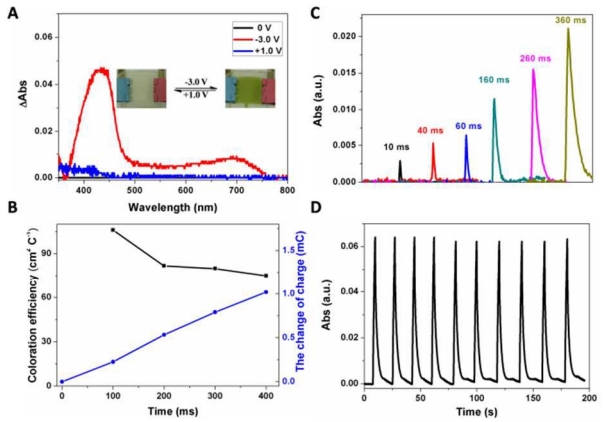


Figure 6 (A) Absorption spectra (black curve) of **M5** in ITO device, stimulated by -3.0 V voltage (red curve), then by +1.0 V voltage (blue curve). inset: The real colour of ITO device stimulated by -3.0 V and +1.0 V voltages. (B) Absorbance change of ITO device stimulated by different switching time. (C) Coloration efficiency of electrochromic device at -3.0 V using ITO device. (D) Absorbance (432 nm) variation of electrochromic device by alternating -3.3 V (2.0 s) and +1.0 V (17s) using ITO device.

4. Conclusions

A novel methyl ketone bridged molecule **M5**, whose photochemical properties can be smartly switched by acid/base, and electrical field, has been synthesized. The colorless **M5** can be switched to green-yellow with broad visible-near infrared absorption (400-500 nm, 550 -800 nm) by base and electricity. The basochromism and electrochromism of **M5** has been studied in detail by cyclic voltammetry (CV), *in-situ* UV-Vis spectroscopy and DFT calculation. The electrochromic mechanism of **M5** containing three electron transfer-three proton transfer processes has been proved. The multi-stimuli color switch has been successfully applied in electrochromic device with a short switching time and good reversibility. In addition, this is another example of application of "electrobase" in situ for molecular switching.

Acknowledgements

This work was supported by the National Science Foundation of China (Grant No. 51373068; No.51303063) and the program of Chang Jiang Scholars and Innovative Research Team in University (IRT101713018) for financial support.

Notes and references

1. B. Xu, Z. Chi, X. Zhang, H. Li, C. Chen, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, 2011, **47**, 11080–11082; K. Cai, Q. Yan, and D. Zhao, *Chem. Sci.*, 2012, **3**, 3175.
2. B. Yang, J. Liu, H. Zheng and S. X.-A. Zhang. *Chin. J. Chem.* 2013, **31**, 1483–1487.
3. J. Sun, X. Lv, P. Wang, Y. Zhang, Y. Dai, Q. Wu, M. Ouyang, C. Zhang. J. Mater. Chem. C, 2014, **2**, 5365-5371.
4. L. Song, Y. Yang, Q. Zhang, H. Tian, W. Zhu, J. Phys. Chem. B, 2011, 115, 14648–14658.
5. P. Singh, A. Baheti, and K. R. J. Thomas. *J. Org. Chem.* 2011, **76**, 6134–6145.
6. M. Gupta, S. Mula, M. Tyagi, T. K. Ghanty, S. Murudkar, A. K. Ray, and S. Chattopadhyay, *Chem. Eur. J.*, 2013, **19**, 17766 – 17772; K. Li, Y. Xiang, X. Wang, J. Li, R. Hu, A. Tong, and B. Z. Tang, *J. Am. Chem. Soc.*, 2014, **136**, 1643−1649; L. Motiei, M. Lahav, D. Freeman and M. E. van der Boom, *J. Am. Chem. Soc.*, 2009, **131**, 3468–3469; P. M. Beaujuge, S. Ellinger, J. R. Reynolds, *Nat. Mater.*, 2008, **7**, 795–799.
7. T. Meyer, K. Hemelsoet, L. Schueren, E. Pauwels, K. Clerck, and Veronique V. Speybroeck, *Chem. Eur. J.*, 2012, **18**, 8120 – 8129; S. Chen, W. Chen, W. Shi, and H. Ma, *Chem. Eur. J.*, 2012, **18**, 925 – 930.
8. S. Zhu, M. Li, L. Sheng, P. Chen, Y. Zhang and S. X. Zhang, *Analyst* 2012, **113**, 5581.
9. D. I. Gittins, D. Bethell, D. J. Schiffrin and R. J. Nichols, *Nature*, 2000, **408**, 67; S. J. van der Molen and P. Liljeroth, *J. Phys.: Condens. Matter.*, 2010, **22**, 133001.
10. P. Xue, R. Lu, J. Jia, M. Takafuji, and H. Ihara, *Chem. Eur. J.*, 2012, **18**, 3549 – 3558; I. Gallardo, G. Guirado, M. Moreno, G. Prats, and M. Takeshita, *Chem. Eur. J.*, 2012, **18**, 9807 – 9812; Z. Zhang, D. Yao, T. Zhou, H. Zhang and Y. Wang, *Chem. Commun.,* 2011, **47**, 7782–7784.
11. C. Dou, L. Han, S. Zhao, H. Zhang, and Y. Wang, *J. Phys. Chem. Lett.*, 2011, **2**, 666–670.
12. S. Sumiya, T. Doi, Y. Shiraishi, and T. Hirai, *Tetrahedron*, 2012, **68,** 690-696; R. H. Mitchell, T. R. Ward, Y. Wang, and P. W. Dibble, *J. Am. Chem. Soc.* 1999, **121**, 2601-2602.
13. K. Higashiguchi, K. Matsuda, and M. Irie, *Angew. Chem. Int. Ed.* 2003, **42**, 3537-3540; K. Higashiguchi, K. Matsuda, M. Matsuo, T. Yamada, and M. Irie, *J. Photochem. Photobiol. A: Chem.,* 2002, **152**, 141-146; K. Higashiguchi, K. Matsuda, N. Tanifuji, and M. Irie, *J. Am. Chem. Soc*. 2005, **127**, 8922-8923.
14. H. Y. Lee, A. Olasz, C. Chen, and D. Lee, *Org. Lett.*, 2012, **14**, 6286–6289.
15. K. Motoyama, H. Li, T. Koike, M. Hatakeyama, S. Yokojima, S. Nakamura and M. Akita, *Dalton Trans.*, 2011, **40**, 10643; J. Massaad, J. Micheau, C. Coudret, R. Sanchez, G. Guirado, and S. Delbaere, *Chem. Eur. J.*, 2012, **18**, 6568 – 6575; R. S. Sánchez, R. Gras-Charles, J. L. Bourdelande, G. Guirado, and J. Hernando, *J. Phys. Chem. C*, 2012, **116**, 7164−7172; W. Zhu, L. Song, Y. Yang, and H. Tian, *Chem. Eur. J.*, 2012, **18**, 13388 – 13394.
16. F. M. Raymo, S. Giordani, *J. Am. Chem. Soc.,* **2001,** *123,* 4651-4652; F. M. Raymo, S. Giordani, *J. Am. Chem. Soc.,* **2002,** 124, 2004-2007; F. M. Raymo, R. J. Alvarado, S. Giordani, M. A. Cejas, *J. Am. Chem. Soc.,* **2003**, 125, 2361-2364; F. M. Raymo, S. Giordani, *J. Org.*

Chem., **2003**, *68*, 4158-4169; S. Zhu, M. Li, S. Tang, Y. Zhang, B. Yang, and S. X. -A Zhang, *Eur. J. Org. Chem.*, 2014, **6**, 1227–1235.

17. Y. M. Zhang, M. Li, W. Li, Z. Huang, S. Zhu, B. Yang, X. Wang, and S. X.-A. Zhang, *J. Mater. Chem. C.*, **2013**, 1, 5309-5314; Y. Zhang, W. Li, X. Wang, B. Yang, M. Li, and S. X.-A. Zhang, C*hem. Commun.*, 2014, **50**, 1420-1422; Y. M. Zhang, X. Wang, W. Zhang, W. Li, X. Fang, B, Yang, M. Li and S. X. A. Zhang, *Light: Science & Aplication*, 2015, **4**, e249.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A. , J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, (Revision A. 02), Gaussian, Inc., Wallingford, CT 2009.
19. C. Friedel, J. M. Crafts. *Compt. Rend.* 1877, **84**, 1392-1450; J. K. Groves. *Chem. Soc. Rev.* 1972, 1, 73-97.
20. R. J. Thomas, K. N. Campbell, G. F. Hennion. *J. Am. Chem. Soc.* 1938, **60**, 718-720; M. Kutscheroff, *Chem. Ber.* 1884, **17**, 13-29; M. Kutscheroff. *Chem. Ber.* 1881, **14**, 1540-1542.
21. H. A. Dieck, and F. R. Heck, *J. Organomet. Chem.* 1975, **93**, 259; K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.* **1975**, 4467.