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Azobenzene-Containing Supramolecular Polymer Films for Laser-Induced Surface Relief Gratings

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We have synthesized a new azobenzene compound hexahexanoyl 4,4′-dimelaminoazobenzene (He-Diazine-Azo) with self-complementary quadruple hydrogen bonds. The azobenzene in He-Diazine-Azo can undergo trans−cis photoisomerization efficiently. Using such a building block, we prepared azobenzene-containing supramolecular polymer films based on multiple hydrogen bonds. In addition, it is found, interestingly, that surface relief gratings can be laser-induced on such azobenzene-containing supramolecular polymer films. The supramolecular polymer films can keep good stability until 100 °C.

Introduction

Research on supramolecular polymers has made rapid progress since the concept was introduced by Lehn.[1−5] The formation of supramolecular polymers can be driven by different intermolecular interactions, including coordination bond, hydrogen bond, $\pi-\pi$ interaction, and so on. Among them, the hydrogen bond is one of the most useful interactions in the fabrication of supramolecular polymers,[5] for its directionality and moderate intensity.[6] For example, a supramolecular main-chain polymer can be formed by triple hydrogen bonds between difunctional diaminopyridines and difunctional uracil derivatives,[7,8] which exhibits liquid crystal behavior over a broad temperature window. One more typical example is the supramolecular polymers formed through self-complementary recognition of the quadruple hydrogen bonds introduced by Meijer et al.[9,10] The supramolecular polymers based on intermolecular interaction are able to behave as reversible and adaptive materials, thus opening a new avenue for advanced soft materials.[11,12]

Azobenzene polymers are a sort of fascinating materials.[13] The incorporation of azobenzene chromophore into the polymers can introduce structural diversity and processible ability into the functional materials. Laser-induced surface relief gratings on azobenzene polymer films have attracted considerable attention since first reported by Natansohn et al. and Tripathy et al. in 1995.[14−17] The formed surface relief gratings are stable when kept below glass transition temperatures. They will be erased by laser or heating.[18−20] Polymers with such properties have shown potential technological applications such as optical information storage and processing, optical switching devices, holographic gratings, and so on. Recently, it was also demonstrated that surface relief gratings could be photoinduced on hyperbranched azo-polymer films[21] and azo derivatives glasses.[22]

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(1) Lehn, J.-M. *Supramolecular Chemistry-Concepts and Perspectives*; VCH: Weinheim, 1995.

(2) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.

(3) Lehn, J.-M. *Polym. Int.* **2002**, *51*, 825−839.

(4) Ciferri, A. *Macromol. Rapid Commun.* **2002**, *23*, 511−529.

(5) Tessa ten Cate, A.; Sijbesma, R. P. *Macromol. Rapid Commun.* **2002**, *23*, 1094−1112.

(6) Jeffrey, G. A. *An introduction to hydrogen bonding*; Oxford University Press: Oxford, 1997.

(7) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254−257.

(8) Lehn, J.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *69*, 1−17.

(9) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lage, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.

(10) Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2003**, 5−16.

(11) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874−878.

(12) Bosman, A. W.; Brunsveld, L.; Folmer, B. J. B.; Sijbesma, R. P.; Meijer, E. W. *Macromol. Symp.* **2003**, *201*, 143−154.

(13) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **l989**, *89*, 1915−1925.

(14) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136−138.

(15) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166−1168.

(16) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817−1845.

(17) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139−4175.

(18) Barrett, C.; Natansohn, A.; Rochon, P. *J. Phys. Chem.* **1996**, *100*, 8836−8842.

(19) Ho, M. S.; Barrett, C.; Paterson, J.; Esteghamatian, M.; Natansohn, A.; Rochon, P. *Macromolecules* **1996**, *29*, 4613−4618.

(20) Jiang, X. L.; Li, L.; Kumar, J.; Kim, D. Y.; Tripathy, S. K. *Appl. Phys. Lett.* **1998**, *72*, 2502−2504.

(21) Che, P. C.; He, Y. N.; Wang, X. G. *Macromolecules* **2005**, *38*, 8657−8663.

(22) Ishow, E.; Lebon, B.; He, Y. N.; Wang, X. G.; Bouteiller, L.; Galmiche, L.; Nakatani, K. *Chem. Mater.* **2006**, *18*, 3693−3697.

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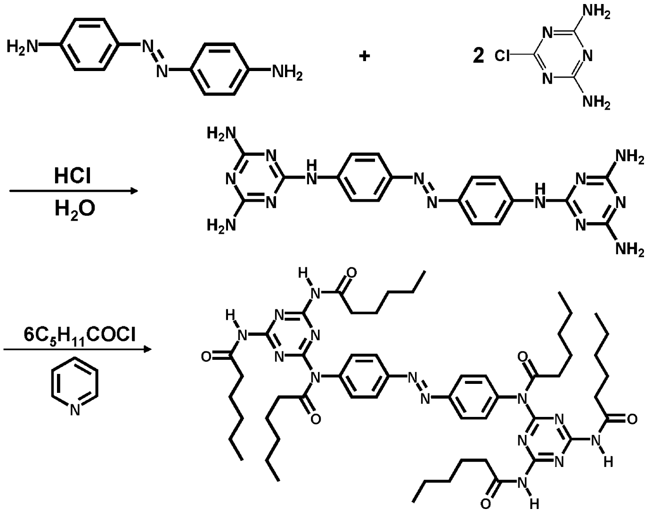
Scheme 1 Routes of Synthesis



For a new application, surface relief gratings were used as templates for soft lithograph.[23]

The noncovalent bond effect has been introduced to prepare side-chain supramolecular azopolymers. Cui and Zhao. have synthesized azopyridine side-chain polymers, and then the amorphous azopyridine polymer can easily be converted into liquid crystalline polymers with aliphatic or aromatic carboxylic acids based on the hydrogen bond.[24] Shibaev et al. have reported for the hydrogen-bonded chiral polymer composites with a frozen cholesteric structure able to respond to changes of pH,[25] and they have also studied the phase behavior and photooptical properties of liquid crystalline functionalized copolymers with azopyridine small molecules stabilized by hydrogen bonds.[26]

In this article, we herein combine the fields of supramolecular polymers and azobenzene polymers in an attempt to develop main-chain supramolecular azobenzene polymers. For this purpose, we need to design and synthesize an azobenzene-containing building block that allows for forming supramolecular azobenzene polymer based on self-complementary quadruple hydrogen bonds. Moreover, we hope this can be used as a series of novel film materials for surface relief gratings and other applications.

Results and Discussion

Synthesis of Building Blocks Bearing Azobenzene and Quadruple Hydrogen-Bonding Donors and Acceptors. The building blocks bearing hydrogen-bonding donors and acceptors have been synthesized as follows. As shown in Scheme 1, 4,4′-dimelaminoazobenzene (Diazine-Azo) was first obtained by reacting two equiv of 2-chloro-4,6-diamino-1,3,5-triazine with 1 equiv of 4,4′-azodianiline in acidic water. Hexahexanoyl 4,4′-dimelaminoazobenzene (He-Diazine-Azo) was then generated by boiling Diazine-Azo with 6 equiv of hexanoyl chloride in refluxing pyridine. When irradiating the He-Diazine-Azo/$CHCl_3$ solution by UV light of 365 nm, as shown in Figure 1, the absorption at 348 nm decreases, and that at 441 nm increases simultaneously. This result indicates that the azobenzene in He-Diazine-Azo can undergo cis−trans photoisomerization efficiently.

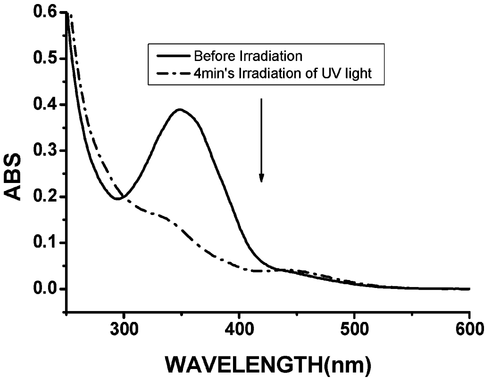


Figure 1. UV spectra of He-Diazine-Azo/$CHCl_3$ solution.

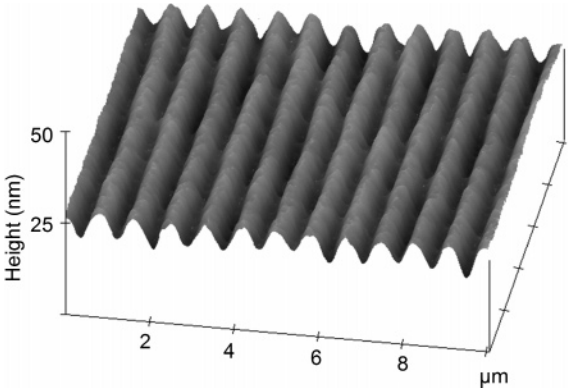


Figure 2. AFM image of the surface relief gratings formed on azobenzene-containing supramolecular polymer film.

Preparation and Characterization of Surface Relief Gratings. The sample was dissolved in dimethylformamide and filtered through 0.45 μm membranes to obtain a solution with the concentration about 0.05 g/mL. The films were prepared by casting the solution onto a clear glass slide and dried at 70 °C under vacuum for 24 h.

We wondered if such azobenzene compound films could be used for surface relief gratings inscription. In doing so, experiments for the fabrication of surface relief gratings were carried out. An Ar^+ laser beam at 488 nm with an intensity of about 100 mW/cm^2 was used as the light source. Surface relief gratings were optically inscribed on the films with p-polarized interfering laser beams, where the Ar^+ laser beam was split by a mirror and the reflected half-beam coincided with the other half on the film surfaces. The surface profiles of the resulting gratings were observed by using a Nanoscope atomic force microscope in the tapping mode. Atomic force microscopy (AFM) observation indicated that sinusoidal surface relief structures with regular spaces were fabricated on the film surfaces of azobenzene-containing supramolecular polymer. Figure 2 shows a typical AFM image of the surface structure formed on the supramolecular polymer films after irradiated for 40 min at room temperature. AFM section analysis shows that the surface modulation depth is about 15 nm, and the grating spacing is about 780 nm.

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(23) Liu, B.; Wang, M. Q.; He, Y. N.; Wang, X. G. *Langmuir* **2006**, *22*, 7405−7410.
(24) Cui, L.; Zhao, Y. *Chem. Mater.* **2004**, *16*, 2076−2082.
(25) Shibaev, P. V.; Schaumburg, K.; Plaksin, V. *Chem. Mater.* **2002**, *14*, 959−961.
(26) Medvedev, A. V.; Barmatov, E. B.; Medvedev, A. S.; Shibaev, V. P.; Ivanov, S. A.; Kozlovsky, M.; Stumpe, J. *Macromolecules* **2005**, *38*, 2223−2229.

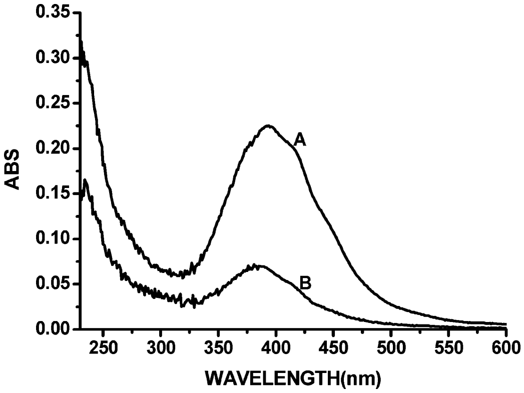


Figure 3. UV−vis spectra of the azobenzene-containing supramolecular polymer film measured after irradiation with a linearly polarized Ar^+ laser beam for 20 min. A: perpendicular to the polarization direction of the laser beam. B: parallel to the polarization direction of the laser beam.

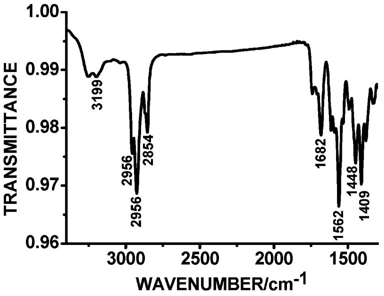
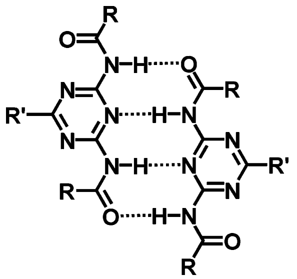


Figure 4. FT-IR transmission spectrum of a He-Diazine-Azo cast film on a CaF_2 slide.

Photoinduced Dichroism. The orientation of azobenzene in the resulting gratings was studied by the polarized UV−vis spectroscopy. After the film was exposed to the linearly polarized Ar^+ laser beam (488 nm, 80 mW/cm^2) for 20 min, significant dichroism was observed. As shown in Figure 3, the absorbance in the direction parallel to the polarization of the laser beam is obviously smaller than that in the direction perpendicular to the polarization of the laser beam. Such a result indicates that the preferential orientation of the azobenzene chromophores is perpendicular to the electric vector of the laser beam. The orientation order parameter S, which is often used to describe the degree of orientation, can be estimated from the dichroic ratio $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, where $A_\perp$ and $A_\parallel$ are the maximum absorbance in directions perpendicular and parallel to the polarization.[27] The orientation order parameter S of this supramolecualr azobenzene film is estimated to be 0.42.

Multiple Hydrogen Bonds. Fourier transform infrared FT-IR was used to confirm the existence of intermolecular quadruple hydrogen bonds in the films. As shown in Figure 4, the band at 1682 cm^{-1} is ascribed to the hydrogen-bonded C═O in the amide groups, and the band at 1741 cm^{-1} close to 1682 cm^{-1} is attributable to the other kind of C═O in the middle of the molecule, which does not have the opportunity to form hydrogen bond. The band at 3199 cm^{-1} indicates that half of the amide groups exist as the cis conformation and in associated states.[28] As a result of the cis conformation of the amide groups, these compounds feature a linear DADA array of four hydrogen-bonding sites. The DADA array of bis-(acylamino)triazine headgroups allows the existence of self-complementary quadruple hydrogen bonds, showing the geometry depicted in Scheme 2. The formation of the hydrogen bond was also supported by NMR. As shown in Supporting Information, the appearance of the NH signal at 10.34 indicates the formation of a strong intermolecular hydrogen bond. Moreover, such a typical proton signal cannot be observed when dissolved in DMSO-d_6 for the reason of the breakage of multiple hydrogen bonds.

Scheme 2 Proposed Geometry of Self-Complementary Quadruple Hydrogen Bonds



Thermal Stability of the Surface Relief Gratings. To test whether the surface relief grating based on such multiple hydrogen-bonding supramolecular polymers can withstand high temperature, we observed the change of the surface profiles on increasing the temperature of the substrate by temperature-dependent AFM. Figure 5 shows the AFM images of surface relief grating at different temperatures. It is found that the surface modulation depth at 60 °C is the same as that observed at room temperature indicated by AFM section analysis, and the supramolecular polymer films still keep good stability until 100 °C. Surface relief gratings become blurry when it was heated to 120 °C and then evidently removed at 150 °C. Therefore, the supramolecular polymer film has demonstrated very good thermal stability, though it is formed based on multiple hydrogen bonds.

It should be noted that the association constant of bis-(acylamino)triazine headgroups is just about 24 M^{-1} in

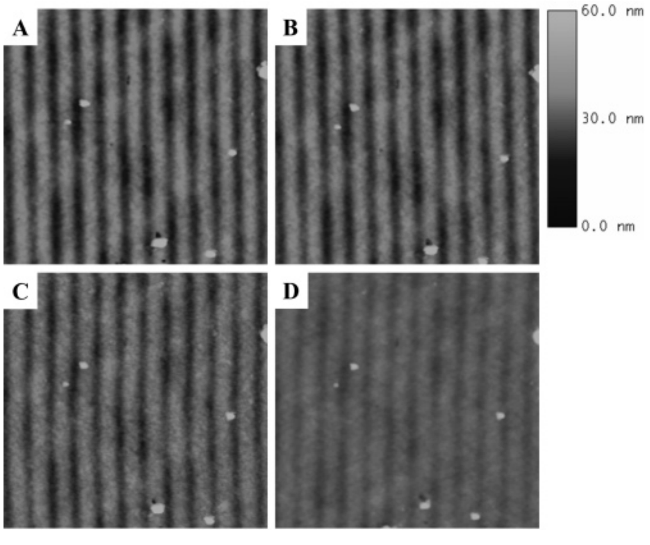


Figure 5. AFM images showing the surface profiles transformation of surface relief gratings on changing the substrate temperature: (A) 60 °C; (B) 100 °C; (C) 120 °C; and (D) 150 °C (the image size is 7.5 μm × 7.5 μm in each case, and each image was recorded in the height mode).

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(27) Wu, Y. L.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A. T.; Shiono, A.; Ikeda, T. *Macromolecules* **1998**, *31*, 349−354.

(28) Beijer, F. H.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W.; Kooijman, H.; Spek, A. L. *J. Org. Chem.* **1996**, *61*, 6371−6380.

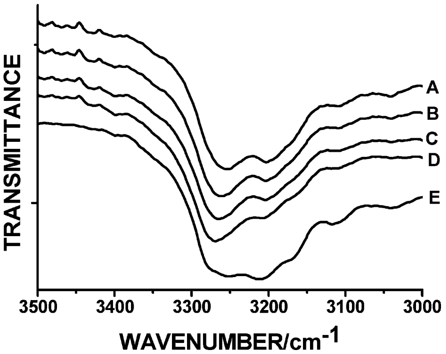

Figure 6. FT-IR transmission spectra of a He-Diazine-Azo cast film on a CaF_2 slide as a function of temperature: (A) 25 °C; (B) 80 °C; (C) 120 °C; (D) 150 °C; and (E) back to 25 °C.

solution.[28] Therefore, high concentration of He-Diazine-Azo is needed if forming the high molecular weight supramolecular polymer in solution. However, for fabricating the solid film of the supramolecular polymer, where the value of the concentration of the monomer is maximized, the requirement for a strong monomer−monomer interaction is yet relaxed. In other words, although the association constant is low, He-Diazine-Azo can still form a high molecular weight supramolecular polymer in solid films. That could be the reason that surface relief gratings on azobenzene-containing supramolecular polymer films have very good thermal stability.

In order to gain more information about the mechanism of thermally induced loss of the gratings, in situ temperature-dependent FT-IR measurements were carried out. As shown in Figure 6, the band around 3200 cm^{-1} is ascribed to the cis conformation of the amide groups, and the band around 3250 cm^{-1} is ascribed to the trans conformation of the amide groups. From Figure 6, we can find that, with an increase in temperature from 25 °C to 150 °C, there is a clear decrease in intensity at 3200 cm^{-1} and increase in intensity at 3250 cm^{-1}. This result indicates that the amide groups of cis conformation at room temperature mostly change into the trans conformation at 150 °C. Once the amide groups change from the cis conformation to the trans conformation, the self-complementary quadruple hydrogen bonds would be broken. With the disassembly of supramolecualr polymers, the surface relief gratings will disappear at high temperature simultaneously. As shown in Figure 6E, upon cooling to 25 °C, the conformation of amide groups changes back to original state. It should be pointed out that heating such material above 150 °C induces the decomposition gradually, and the decomposition becomes serious at 330 °C.

Conclusions

In summary, we have provided a new approach for fabricating an azobenzene-containing supramolecular polymer film based on multiple hydrogen bonds and demonstrated that such a film can be used for surface relief gratings. The surface relief gratings can keep good stability until 100 °C. Although the supramolecular polymer is a well-established concept, we hope that this line of research may open new avenues for photoresponsive supramolecular polymers.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature on a JEOL JNM-ECA300 (300 MHz) spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. LC-MS measurements were performed on a Thermo Electron Corporation Finnigan LTQ mass spectrum. Infrared spectra were run on a Bruker IFS 66v/s spectrophotometer. UV−vis spectra were performed on a Hitachi U-3010 spectrophotometer. Thermal properties were performed by a Mettler-Toledo DSC821e differential scanning calorimeter. The heating rate of 20 °C/min was used for the differential scanning calorimetry measurements. A commercial multimode Nanoscope IV atomic force microscope was used to investigate the surface profiles of the resulting gratings.

Materials. 2-Chloro-4,6-diamino-1,3,5-triazine was purchased from Aldrich. 4,4′-Azodianiline was purchased from ACROS. Hexanoyl chloride was purchased from Lancaster. Other chemicals were analytically pure. The solvents used were all freshly distilled.

Diazine-Azo. 2-Chloro-4,6-diamino-1,3,5-triazine (1.04 g) was dissolved in 25 mL of H_2O and 3 mL of a solution of 2 M HCl was added. The mixture was stirred at 40 °C for 30 min, 4,4′-azodianiline (0.75 g) was then added, and the mixture was heated at 100 °C for 5 h, after which it was cooled to room temperature. It was neutralized with a solution of 1 M NaOH. A yellow solid was filtered off and dried under vacuum (1.5 g, 84% yield). ^1H NMR (DMSO-d_6): δ 6.40 (s, 8H, $-NH_2$), 7.75 (d, 4H, ArH), 8.00 (d, 4H, ArH), 9.26 (s, 2H, −NH−). ^{13}C NMR (DMSO-d_6): δ 119.64, 123.47, 143.87, 146.81, 165.10, 167.50. LC-MS (MW = 430.18) *m/z* 431.22 $[M]^+$.

He-Diazine-Azo. To a suspension of 4,4′-dimelaminoazobenzene (0.505 g) in boiling dry pyridine (50 mL) was added hexanoyl chloride (1.5 mL) slowly. The reaction mixture was refluxed for 24 h. Then the mixture was cooled to room temperature, and addition of ethyl acetate (100 mL) gave a suspension that was filtered. The filtrate was evaporated. After extraction with CH_2Cl_2 and $NaHCO_3$(aq), with CH_2Cl_2 and H_2O sequentially, CH_2Cl_2 was evaporated. Using column chromatography (VCH_2Cl_2/VCH_3OH = 10:1), pure product was obtained. ^1H NMR ($CDCl_3$): δ 0.83 (t, 12H, −CH3), 0.90 (t, 6H, −CH3), 1.12−1.81 (m, 36H, $-CH_2-$), 2.40 (t, 8H, $-CH_2-$), 3.40 (t, 4H, $-CH_2-$), 7.30 (d, 4H, ArH), 8.02 (d, 4H, ArH), 10.34 (s, 4H, −NH−). ^{13}C NMR ($CDCl_3$): δ 14.03, 14.09, 22.56, 22.62, 24.17, 25.14, 31.32, 31.50, 37.54, 39.44, 124.13, 129.78, 143.09, 151.69, 163.78, 167.14, 176.84, 178.54. LC-MS (MW = 1018.62) *m/z* 1017.62 $[M]^-$.

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Supporting Information Available: ^1H NMR spectra of He-Diazine-Azo/$CHCl_3$ solution; TGA and DSC of He-Diazine-Azo (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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