Supporting Information

Photoresponsive Zn^{2+}-Specific Metallohydrogels Coassembled from Imidazole Containing Phenylalanine and Arylazopyrazoles Derivatives

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1. Experimental Section

a. Materials and Methods

All reactions were carried out under nitrogen on standard vacuum line. All chemicals and solvents were purchased from commercial sources and used as received. Phenylalanine (Phe), sodium borohydride ($NaBH_4$), 1-H-imidazole-2-carbaldehyde, N-methylhydrazine, hydrazine monohydrate, 2-hydrazinoethanol, ethyl-4-aminobenzoate, and ethyl-chloropropionate were purchased form Sigma Aldrich and were used without further purification. All other reagents were of analytical grade, which include Na_2CO_3, $ZnSO_4.6H_2O$, $ZnCl_2$, $Zn(NO_3)_2.6H_2O$, $Zn(OAC)_2.6H_2O$. Deionized water (MillQ, 18.2 MΩ).

b. Instrumentation

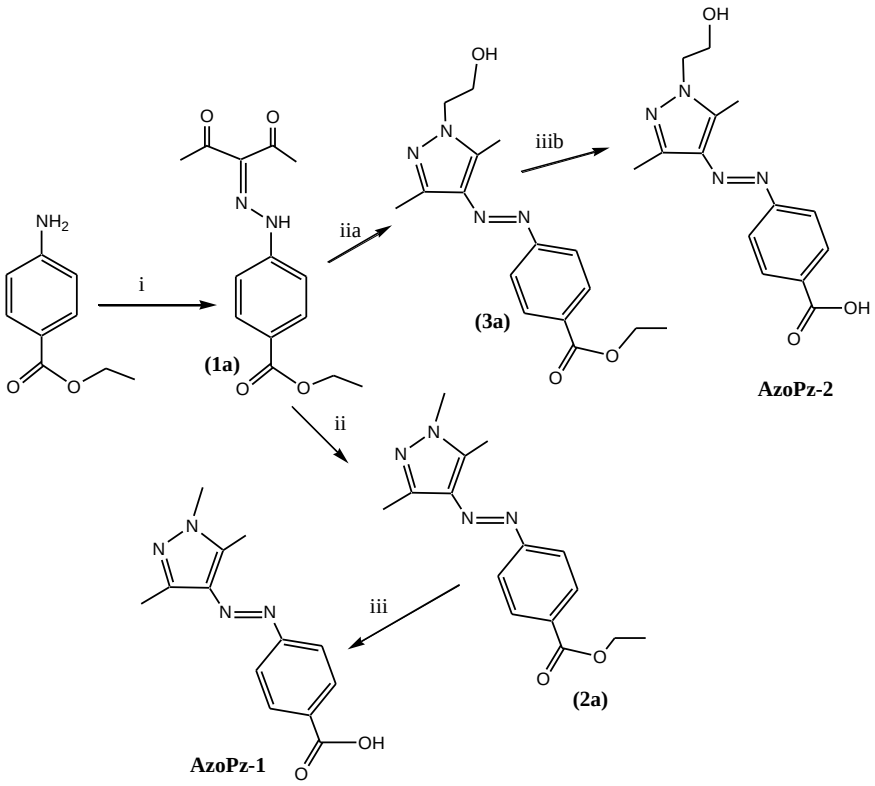
^1H and ^{13}C NMR spectra were recorded on a JEOL Eclipse2-400 MHz spectrometer using solvent resonances as internal references relative to TMS. UV-visible absorption spectra were recorded on a Varian Cary 60 BIO spectrometer from Agilent technologies. Photoisomerization was induced by irradiating solutions of the molecular switches in a quartz cuvette at room temperature with UV light at 365 nm, followed immediately by recording the absorption spectrum. Dry dichloromethane (DCM) or dimethylsulfoxide (DMSO) solvents were used for all UV-visible measurements. FTIR spectra were recorded in KBr pellet using JASCO 4200 series instrument. Transmission electron microscopy images were recorded on a JEOL 1230 instrument at an accelerated voltage of 200 kV. Dynamic Rheological measurements were for the gels were performed on MCR302 rheometer (Anton Paar instrument). The hybrid gels were scooped, placed over the rheometer plate, and allowed to equilibrate for 15 min. The temperature of the

plates was maintained at 25 °C. All rheological experiments were carried out 3 times. The X-ray powder diffraction data (PXRD) was collected in a Bruker AXS, D2 Phaser powder diffractometer using Cu Kα radiation in the 2θ-theta interval 2- 60 degrees. The mass spec analysis was completed using positive-ion mode electrospray ionization with an Apollo II ion source on a Bruker 10 Tesla APEX -Qe FTICR-MS.

2. Synthetic Procedures

2a) Synthesis of the molecular switches AzoPz-1 and AzoPz-2

The precursor compounds (**1a-2a**) and (**1b-2b**) and the final photoswitchable compounds **AzoPz-1** and **AzoPz-2** were synthesized following literature procedures.[1-4]



Scheme S1. Synthetic route for AzoPz-1 and AzoPz-2. i) a) Conc. HCl, AcOH, H_2O, $NaNO_2$, 0 °C; b) EtOH, H_2O, NaOAc, 2,4-pentandione, RT; ii) N-Methylhydrazine, EtOH, reflux; iii) EtOH, H_2O, 1 M NaOH, RT; iiia) EtOH, 2-hydrazinoethanol, reflux; iiib) EtOH, H_2O, 1 M NaOH, RT.

Ethyl-4-(2-(2,4-dioxopentan-3-ylidene)hydrazono)benzoate (1a): A solution of ethyl-4-aminobenzoate (1.22 g, 7.4 mmol) in 10.0 mL of glacial acetic acid and 1.7 mL of HCl was prepared. To this solution, $NaNO_2$ (0.61 g, 8.88 mmol) dissolved in 2.5 mL of H_2O was added dropwise at 0 °C. The reaction mixture was stirred for 1 hour at 0 °C. A suspension of 2,4-pentadione (0.98 mL, 10.0 mmol) and NaOAc (1.81 g, 22 mmol) in 7.0 mL of EtOH and 4.0 mL of H_2O was added dropwise to the above reaction mixture. The resulting mixture was stirred for 1 hour at room temperature. All solvents were removed by rotary evaporation yielding a bright yellow solid in quantitative yield which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 14.54 (s, br, 1H), 8.12 (m, 2H), 7.46 (m, 2H), 4.39 (q, J = 7.1 Hz, 2H), 2.65 (s, 3H), 2.48 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 Hz, $CDCl_3$, ppm) δ: 198.2, 197.0, 165.6, 144.9, 134.2, 131.3, 127.4, 115.7, 61.3, 31.8, 26.7, 14.5.

Ethyl-4-((1,3,5-trimethyl-1H-pyrazol-4-yl)diazenyl)benzoate (**2a**): N-Methylhydrazine (0.89 mL, 18.2 mmol, 1.2 eq) was added to a solution of Ethyl-4-(2-(2,4-dioxopentan-3-ylidene)hydrazono)benzoate(**1**) (3.10 g, 15.2 mmol, 1 eq) in EtOH (100 mL) and was refluxed overnight. The reaction mixture was concentrated under reduced pressure to afford **2** as orange solid in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.13 (d, J = 8.7 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.75 (s, 3H), 2.59 (s, 3H), 2.50 (s, 3H), 1.45 (t J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 166.5, 156.4, 142.8, 139.8, 135.6, 130.6, 130.2, 121.6, 61.1, 36.1, 14.2, 14.0, 10.1.

4-((1,3,5-Trimethyl-1H-pyrazol-4-yl)diazenyl)benzoic acid (AzoPz-1): Ethyl-4-((1,3,5-trimethyl-1H-pyrazol-4-yl)diazenyl)benzoate (**2**) (0.50 g, 1.75 mmol), was dissolved in 100 mL EtOH and 10 mL of 1 M NaOH. The reaction mixture was stirred for 24 hour at room temperature. The reaction mixture was acidified with 1 M HCl and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with 60 mL of H_2O and 30 mL of brine. Then the solvent was removed by rotary evaporation to give the desired product as an orange solid in quantitative yield.

^{1}H-NMR (400 MHz, $CDCl_3$ ppm) δ: 14.58 (s, 1H), 8.08 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 3.92 (s, 3H), 2.61 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 Hz, $CDCl_3$, ppm) δ: 166.8, 156.4, 142.8, 139.8, 135.6, 130.6, 130.2, 121.6, 36.1, 14.0, 10.1. Anal. calculated for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.63; N, 21.70. Found: C, 60.21; H, 5.58; N, 21.40.

Ethyl-4-((1-ethanol-3,5-dimethyl-4-(phenyldiazenyl)-pyrazol-1-yl)benzoate (3a): 4-(2-(2,4-dioxopentan-3-ylidene)hydrazono)benzoate (**1a**) (0.80 g) was dissolved in 25 mL of absolute ethanol. To this solution 2-hydrazinoethanol (0.20 mL, 1.3 mmol) was added dropwise at room temperature. Then, the reaction mixture was refluxed for 4.0 hours. The solvent was removed by rotary evaporation to afford orange solid of the desired product (0.75 g, 82%).

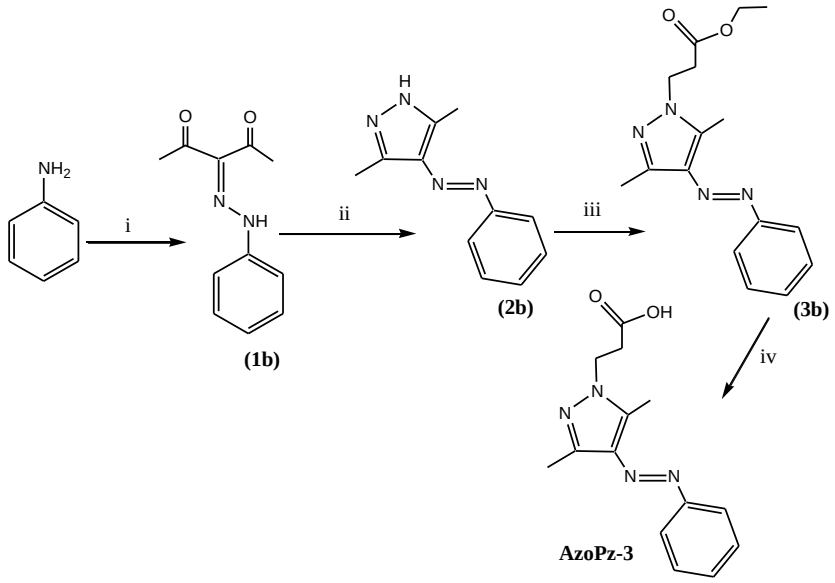
^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 8.11 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 4.39 (q, J = 6.9 Hz, 2H), 4.14 (t, J = 8.7 Hz, 2H), 4.04 (t, J = 8.7 Hz, 2H), 2.61 (s, 3H), 2.48 (s, 3H), 1.41 (t, J = 8.7 Hz, 3H). ^{13}C-NMR (100 Hz, $CDCl_3$, ppm) δ: 166.3, 156.1, 143.0, 140.5, 135.3, 131.0, 130.5, 121.5, 61.3, 61.1, 50.3, 14.3, 14.1, 9.9. Anal. calculated for $C_{16}H_{20}N_4O_3$: C, 60.74; H, 6.37; N, 17.71. Found: C, 60.49; H, 6.31; N, 17.35.

Ethyl-4-((1-ethanol-3, 5-dimethyl-4-(phenyldiazenyl)-pyrazol-1-yl) benzoic acid (AzoPz-2): Ethyl-4-((1-ethanol-3,5-trimethyl-1H-pyrazol-4-yl)diazenyl)benzoate (**3a**) (0.50 g, 1.75 mmol), was dissolved in 100 mL EtOH and 10 mL of 1 M NaOH. The reaction mixture was stirred for 24 hour at room temperature. The reaction mixture was acidified with 1 M HCl and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with 60 mL of H_2O and 30 of brine. Then, the solvent was removed by rotary evaporation to give the desired product as an orange solid in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.13 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 4.16 (t, J = 5.0 Hz, 2H), 4.06 (t, J = 5.0 Hz, 2H), 2.61 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 Hz, $CDCl_3$, ppm) δ: 166.3, 156.2, 140.4, 135.3, 131.1, 130.7, 130.4, 121.6, 61.4, 50.2, 14.3, 14.1. Anal. calculated for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.44. Found: C, 58.10; H, 5.54; N, 19.09.

2b) Synthesis of the molecular switch AzoPz-3

3-(2-phenylhydrazono)pentane-2,4-dione (**1b**): Aniline (1.35 mL, 14.8 mmol, 1.0 eq) was dissolved in AcOH (20 mL) and 12 M HCl (3.40 mL) at 0 °C. $NaNO_2$ (1.23 g, 17.9 mmol, 1.2 eq) dissolved in 5 mL of H_2O was added dropwise to the acidic aniline solution and stirred for 1 hour at 0 °C. A suspension of 2,4-pentadione (1.98 mL, 19.24 mmol) and NaOAc (3.64 g, 44.4



Scheme S2. Synthetic route for AzoPz-3. i) a) Conc. HCl, AcOH, H_2O, $NaNO_2$, 0 °C; b) EtOH, H_2O, NaOAc, 2,4-pentandione, RT; ii) Hydrazine monohydrate, EtOH, reflux; iii) EtOH, Ethyl 3-chloropropionate, reflux; iv) EtOH, H_2O, 1 M NaOH, RT.

mmol in 14 mL of EtOH and 8 mL of H_2O was prepared and the aniline mixture was added dropwise to the suspension forming a yellow precipitate immediately. The reaction mixture was stirred for 1 hour at room temperature. The yellow precipitate was collected by filtration and washed with a 1:1 mixture of H_2O and EtOH and then with a small amount of hexanes. The product was air dried overnight to afford **1b** as a yellow solid (2.39 g, 81%).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 14.70 (br s, 1H), 7.43 (m, 4H), 7.21 (m, 1H), 2.62 (s, 3H), 2.51 (s, 3H).^{13}C NMR (100 $MH_{Z,}$ $CDCl_3$) (δ ppm): 198.0, 197.1, 141.6, 133.3, 129.7, 125.9, 116.3, 31.7, 14.4, 9.8.

3,5-Dimethyl-4-(phenyldiazenyl)-1H-pyrazole (**2b**): Hydrazine monohydrate (0.89 mL, 18.2 mmol, 1.2 eq) was added to a solution of 3-(2-phenylhydrazono) pentane-2,4-dione (**1b**) (3.10 g, 15.2 mmol, 1 eq) in EtOH (125 mL) and was refluxed overnight. The reaction mixture was concentrated under reduced pressure to afford **2b** as an orange solid in quantitative yield.

^{1}H NMR (400MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.1 (s, br, 1H), 7.80 (d, ^{2}J = 7.3 Hz, 2H), 7.41-7.49 (m, 3H), 2.8 (s, 6H, CH_3). ^{13}C NMR (100 MHz, ppm) δ : 152.76, 131.42, 140.6, 129.4, 122.5, 11.1.

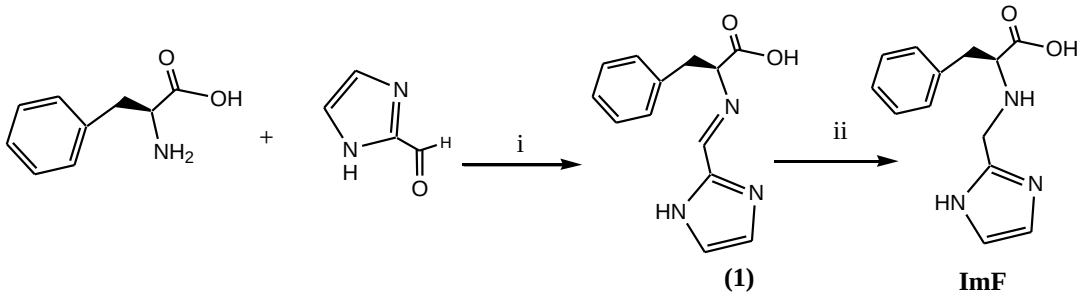
Ethyl-3-((3,5-dimethyl-4-(phenyldiazenyl)-pyrazol-1-yl)-propionate (**3b**): Anhydrous K_2CO_3 (0.486 g, 2.94 mmol, 1.2 eq) was added to a solution of (3,5-dimethyl-4-(phenyldiazenyl)-1H-pyrazole (**2b**) (0.491g, 2.45 mmol, 1 eq) in MeCN (10.0 mL). Afterwards, ethyl 3-

chloropropionate (0.338 mL, 2.45 mmol, 1 eq) was added. The resulting mixture was refluxed and stirred overnight. It was then allowed to cool to room temperature and the solvent was removed under reduced pressure to afford an orange solid of the desired product (**3**) that was used without further purification. (1.36 g, 71.9%) ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.13 (d, J = 8.7 Hz, 2H), 7.80 (d J = 8.7 Hz, 2H), 4.40 (q, J = 6.8 Hz, 2H), 4.16 (t, J = 5.0 Hz, 2H) 4.06 (t, J = 5.0 Hz, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 1.42 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 166.3, 156.1, 143.0, 140.5, 135.3, 131.0, 130.5, 121.5, 61.3, 61.1, 14.3, 14.1, 9.85. Anal. calculated for $C_{16}H_{20}N_4O_2$: C, 63.98; H, 6.71; N, 18.66. Found: C, 63.72; H, 6.65; N, 18.29.

3-(3,5-Dimethyl-4-(phenyldiazenyl)-pyrazol-1-yl)-propionic acid (**AzoPz-3**): Ethyl-3-((3,5-Dimethyl-4-(phenyldiazenyl)-pyrazol-1-yl)-propionate (**3**) (0.74 g, 2.46 mmol, 1 eq) was dissolved in 100 mL of EtOH and 10 mL 1 M aqueous NaOH solution. The resulting reaction mixture was stirred overnight at room temperature. Afterwards, the mixture was acidified with 1 M HCl, and extracted with (3 x 20 mL) ethyl acetate. The combined organic layers were washed with 100 mL of water and 50 mL of brine and dried over Na_2SO_4. The solution was filtered and then concentrated under reduced pressure to afford an orange solid of the desired product (0.85 g, 95% yield).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.80-7.77 (m, 2H), 7.47-7.45 (m, 3H), 4.34 (t, J = 6.0 Hz, 2H), 3.94 (t, J = 6.0 Hz, 2H), 2.66 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 174.4, 153.5, 143.0, 139.4, 135.0, 129.6, 129.0, 121.9, 43.6, 34.4, 14.0, 9.8. Anal. calculated for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.56. Found: C, 61.51; H, 5.88; N, 20.26.

2c) Synthesis of the ImF gelator

N-(1-H-imidazol-4-yl)methylidene-L-phenylalanine gelator (ImF). The compound ImF was prepared following a slightly modified literature procedure.[4] To an aqueous solution (10 mL) of Phe (0.83 g, 5 mM) containing Na_2CO_3 (0.53 g, 5 mM), 1-H-Imidazole-2-carbaldehyde (0.48 g, 5 mM) in ethanol (5 mL) was added slowly. The mixture was stirred for 3 h at 50 °C. Then, the solution was cooled in an ice bath. $NaBH_4$ (0.23 g, 6 mM) was slowly added to the above solution. The mixture was stirred for 3 h, and 6 M hydrochloric acid was added to neutralize the basic (pH ~ 10) reaction mixture and the pH was adjusted to 5.0-6.0. The reaction mixture was stirred further for 2 h. The resulting solid was filtered off and was washed with ethanol and water, then air dried to give the desired as a white solid (1.12 g, 91%).
^{1}H-NMR (400 MHz, D_2O, ppm) δ: 7.40-7.27 (m, 5H), 7.05 (s, 2H), 3.77 (dd, J = 7.1 Hz, 1H, CH_2), 3.37 (t, J = 6.9 Hz, 1H, CH), 2.94 (d, J = 6.8 Hz, 2H, CH_2). ^{13}C-NMR (400 MHz, D_2O, ppm) δ: 180.7, 146.4, 138.0, 129.3, 128.6, 126.7, 122.0, 64.8, 43.9, 39.1. Anal. calculated for $C_{13}H_{15}N_3O_2$: C, 63.65; H, 6.16; N, 17.14. Found: C, 63.40; H, 6.10; N, 16.80.



Scheme S3. Synthetic route for ImF. i) EtOH, Na_2CO_3, 50 C; ii) $NaBH_4$,0 °C.

3. NMR Spectra of AzoPz1-3 and ImF

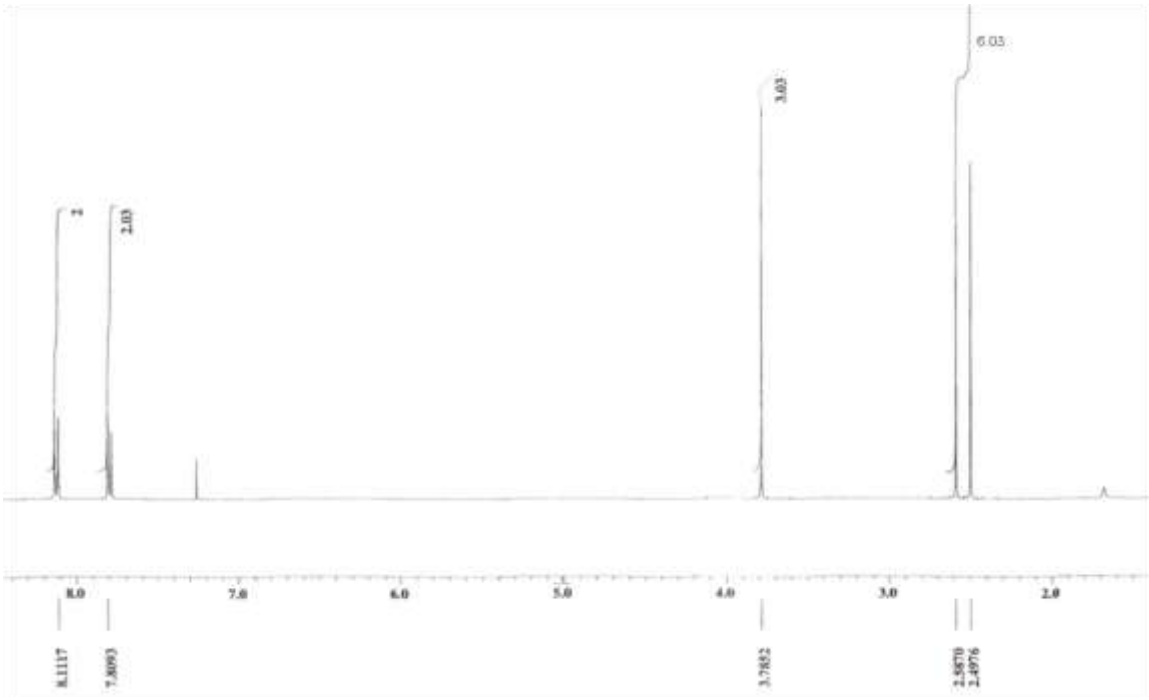


Fig. S1. ^{1}H NMR (400 MHz) spectrum of the photoswitchable compound **AzoPz-1** in $CDCl_3$.

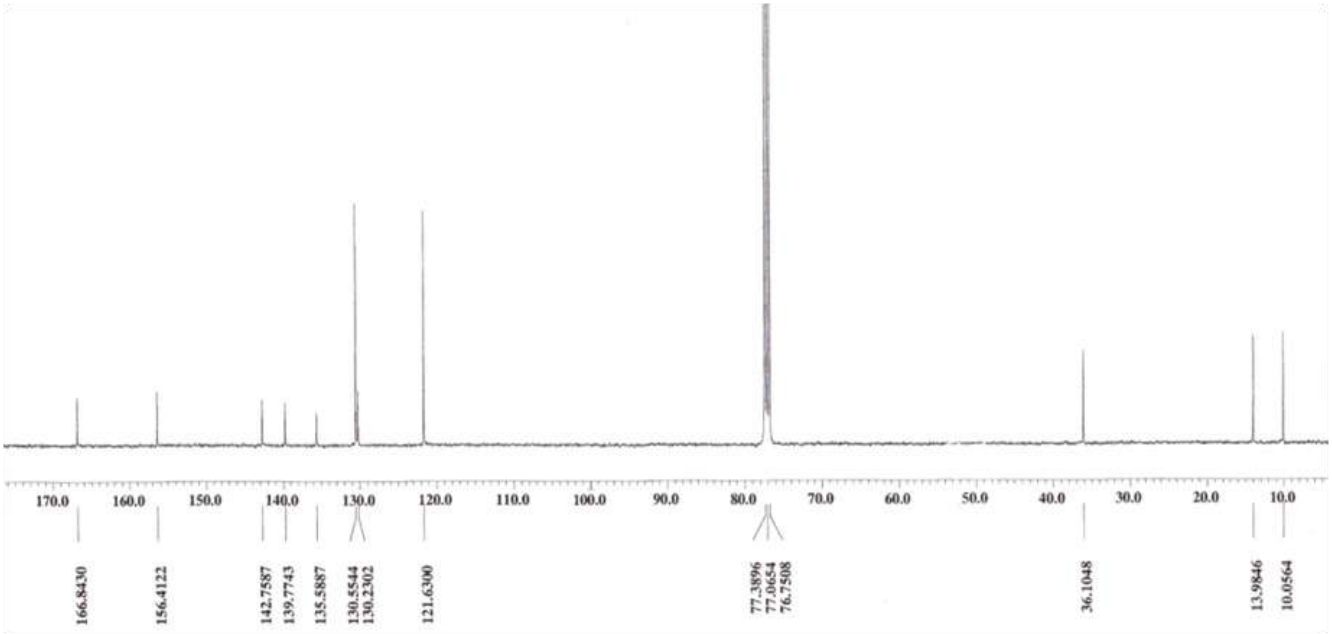


Fig. S2. ^{13}C NMR (100 MHz) spectrum of the photoswitchable compound **AzoPz-1** in $CDCl_3$.

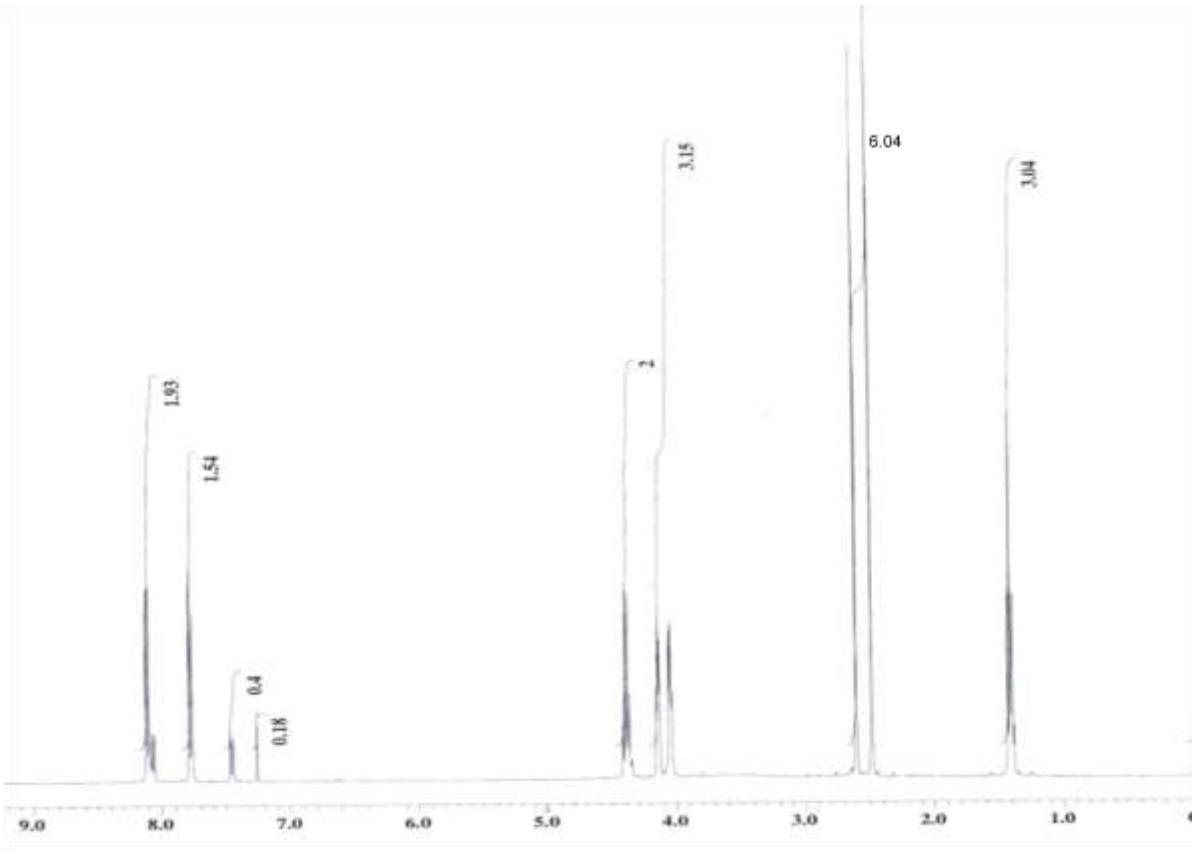


Fig. S3. ^{1}H NMR (400 MHz) spectrum of the intermediate compound **3a** in $CDCl_3$.

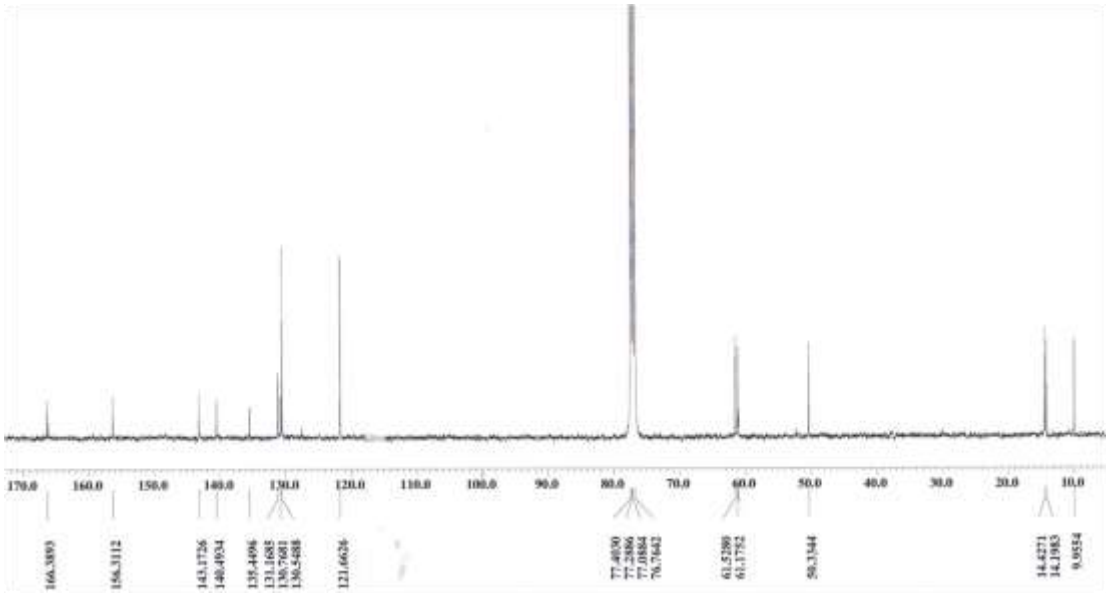


Fig. S4. ^{13}C NMR (100 MHz) spectrum of intermediate compound **3a** in $CDCl_3$.

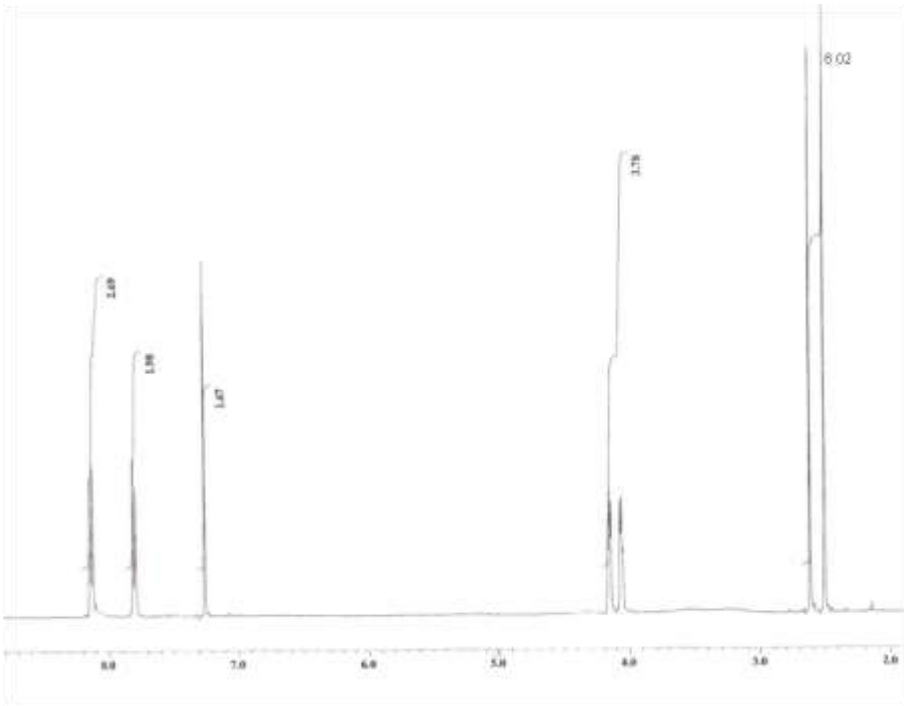


Fig. S5. ^{1}H NMR (400 MHz) spectrum of the photoswitchable compound **AzoPz-2** in $CDCl_3$.

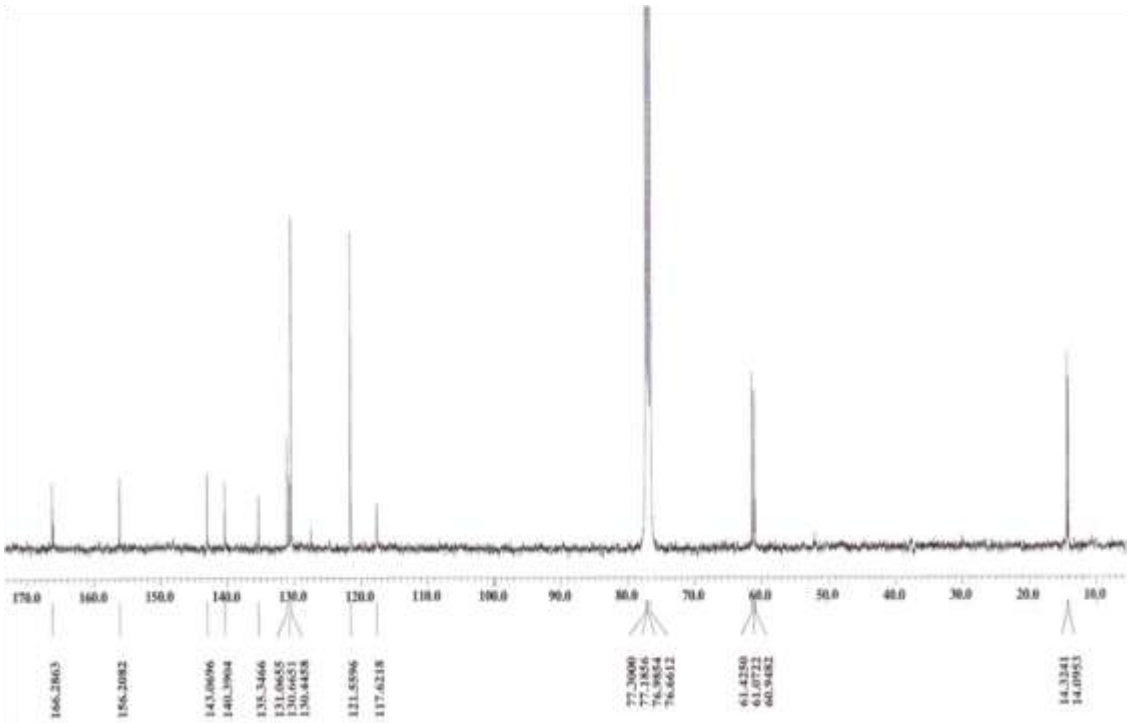


Fig. S6. ^{13}C NMR (100 MHz) spectrum of the photoswitchable compound **AzoPz-2** in $CDCl_3$.

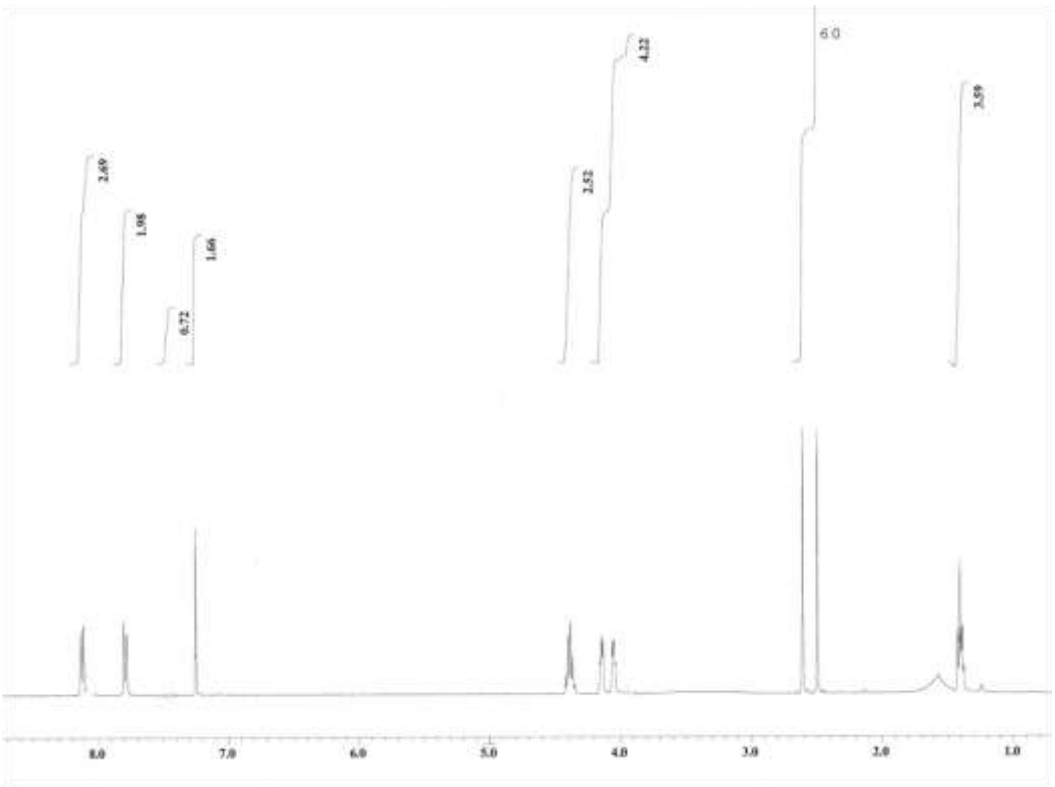


Fig. S7. ^{1}H NMR (400 MHz) spectrum of the intermediate compound **3b** in $CDCl_3$.

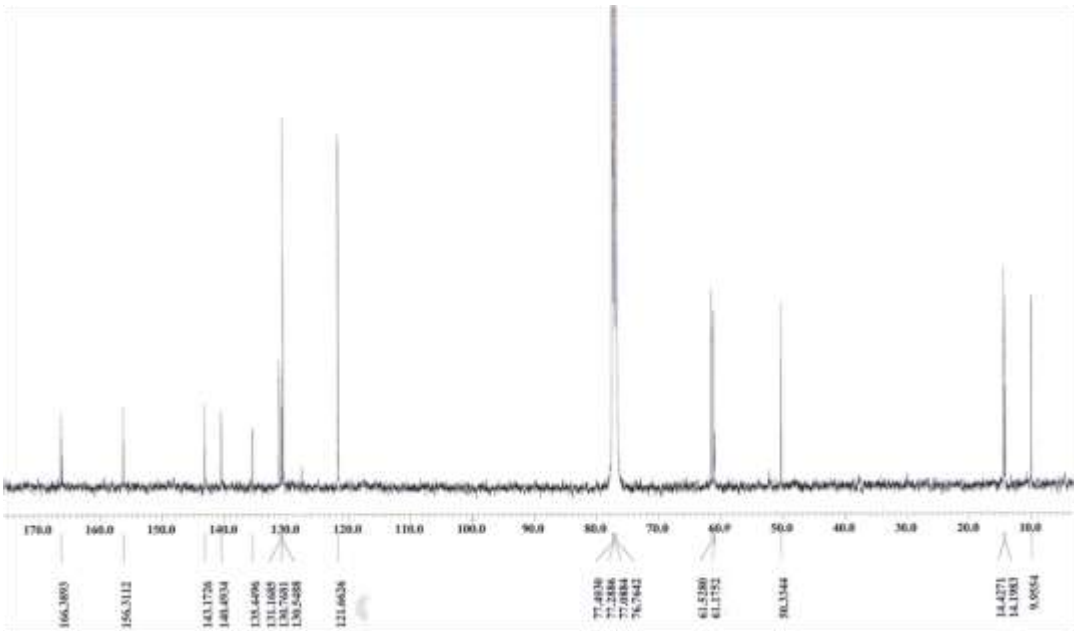


Fig. S8. ^{13}C NMR (100 MHz) spectrum of the intermediate compound **3b** in $CDCl_3$.

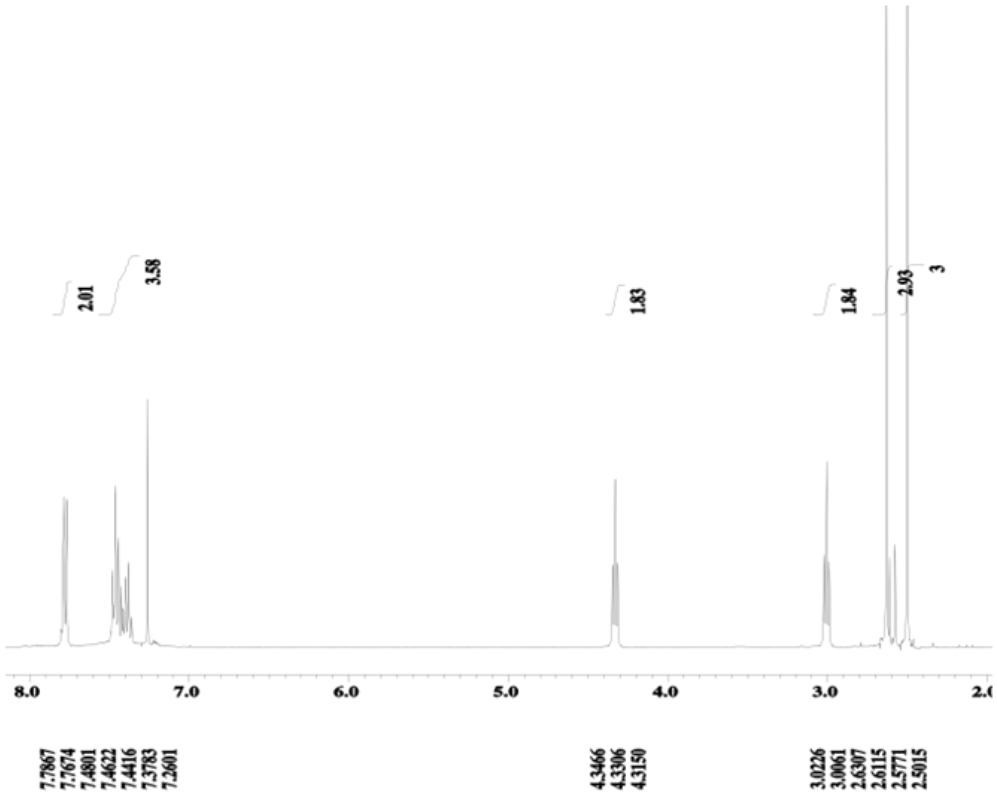


Fig. S9. ^{1}H NMR (400 MHz) spectrum of the photoswitchable compound **AzoPz-3** in $CDCl_3$.

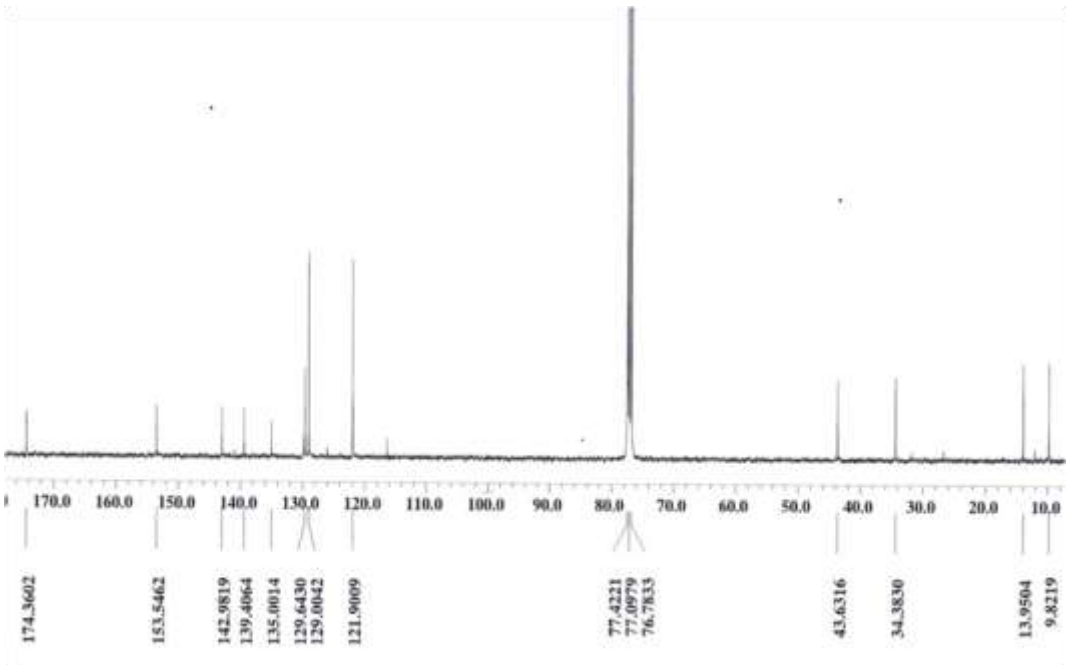


Fig. S10. ^{13}C NMR (100 MHz) spectrum of the photoswitchable compound **AzoPz-3** in $CDCl_3$.

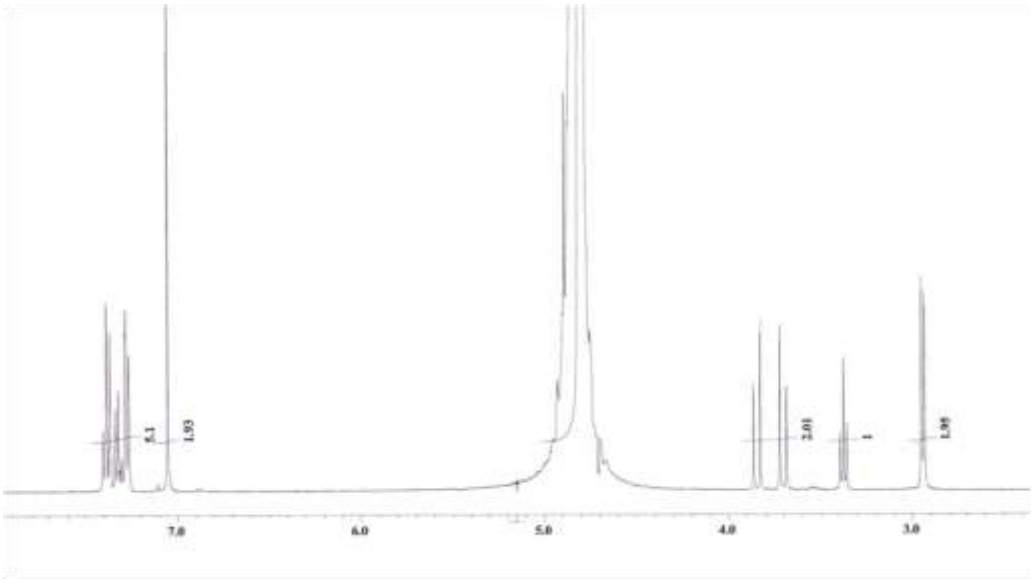


Fig. S11. ^{1}H NMR (400 MHz) spectrum of the gelator compound ImF in D_2O.

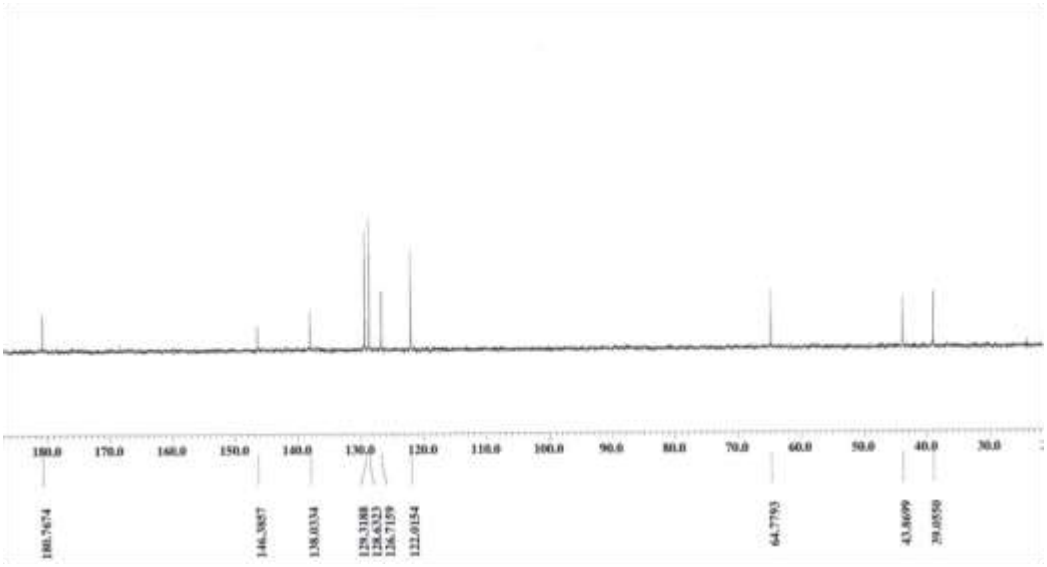


Fig. S12. ^{13}C NMR (100 MHz) spectrum of the gelator compound ImF in D_2O.

4. Preparation of Zn-ImF gels

In a typical experiment, a stock solution of the ImF (50 mM) was prepared in deionized water by adding NaOH (1 M) to adjust the pH until the gelator was completely dissolved (pH ~ 8-11). Similarly, a solution of $ZnCl_2$, (50 mM) was prepared by dissolving in deionized water. Then, appropriate amount of the ImF solution was placed in a glass vial, and 0.50 equiv of the $ZnCl_2$ solution in water is added to reach a final volume of 1.0 mL. The mixture was changed into a white metallohydrogel after vortex treatment for 10 min at room temperature. Samples were defined as gels if the inverted-vial test was passed.

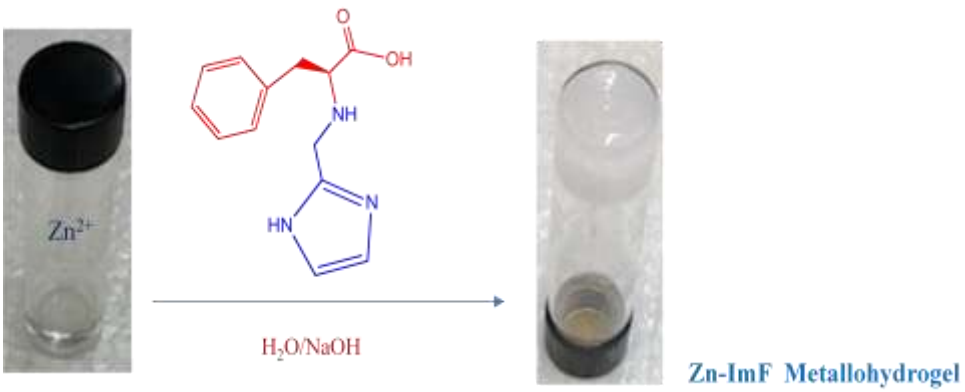


Fig. S13. Molecular structure of the ImF gelator and the formation of the Zn-ImF metallohydrogel in a 2:1 ImF:Zn^{2+} mole ratio.

Effect of anions on gelation: The effect of anions on gelation was studied by using $Zn(NO_3)_2.6H_2O$, $Zn(CH_3CO_2)_2.2H_2O$, $ZnSO_4.6H_2O$ salts instead of $ZnCl_2$ under the same conditions. The results showed that all zinc salts induce the formation of metallohydrogels, suggesting anions have no influence in the gelation process (Table S1).

Table S1. Metallogel formation with various Zinc (II) salts and ImF in a 2:1 mole ratio.

Phase	Time	Metal salt used
Gel (**1**)	3 min	$Zn(O_2CH_2CH_3)_2$
Gel (**2**)	2 min	ZnSO4
Gel (**3**)	2 min	$ZnCl_2$
Gel (**4**)	3 min	$Zn(NO_3)_2$

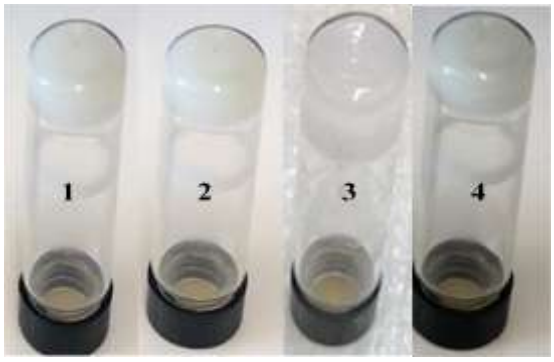


Fig. S14. Digital photos of the Zn-ImF metallohydrogels in the presence of different zinc salts.

Effect of cations on gelation: To probe the effect of metal ions on gelation various metal salts were tested following the same procedure as described above for the preparation zinc metallohydrogels. The results revealed that the gelation process is cation specific, i.e., gel formation occurred in the presence of zinc salts only. All the other metal ions tested furnished either clear solutions or precipitates.

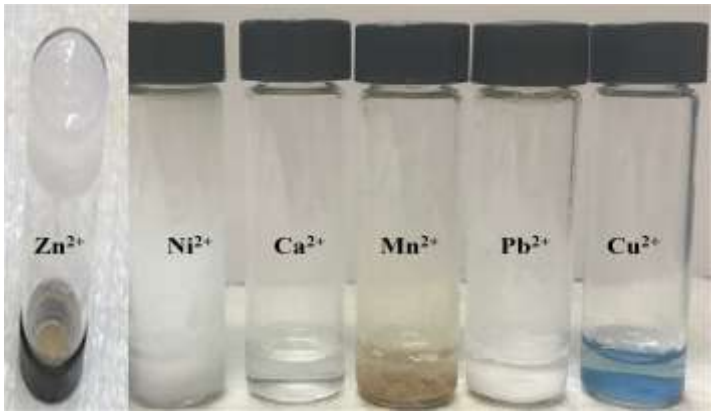


Fig. S15. Optical images of ImF in combination with different metal ions.

Preparation of the photoresponsive Zn-ImF-AzoPz1-3 gels: The photoswitchable gels were prepared in manner to the Zn-ImF gels. First, a stock solution of the ImF (50 mM) was prepared in deionized water by adding NaOH (1 M) to adjust the pH until the gelator was completely dissolved (pH ~ 8-11). Then, solutions of $ZnCl_2$, (50 mM) and AzoPz-1 (50 mM) were prepared by dissolving in deionized water and DMSO, respectively. Then, appropriate amount of the ImF solution was placed in a glass vial, and 0.50 equiv of the $ZnCl_2$ solution in water and 0.25 equiv AzoPz-1 were added successively to reach a final volume of 1.0 mL. The mixture was changed into an orange metallogel after vortex treatment for 10 min at room temperature. Samples were defined as gels if the inverted-vial test was passed. The same procedures were used for preparing of the gels using the AzoPz-2 and AzoPz-3 photoswitches.

Fig. S16. Formation of the hybrid photoresponsive Zn-ImF-AzoPzs metallogel coassembly.

5. UV-vis spectra of Azopz1-3 and metallogels

UV-Vis absorption spectral changes of the photoswitchale compounds were recorded in DMSO solution in a quartz cuvettes (1.0 cm path length) on Cary Bio 60 spectrophotometer from

Agilent technologies, followed immediately by recording the absorption spectrum. Dry dichloromethane (DCM) or dimethylsulfoxide (DMSO) solvents were used for all UV-visible measurements.

Photoswitching Experiments. The trans-to-cis photoisomerization was induced by irradiating solutions of the samples in a quartz cuvette at room temperature with UV light (λ = 365 nm). The reverse cis-to-trans photoisomerization experiments was conducted by irradiating solutions of the samples with green light (λ = 530 nm) using the LSC-G high Powered-LED Rayonet photochemical reactor (The Southern New England Ultraviolet Company). The extent of isomerization at the photostationary state is estimated based on the following difference equation:

$$\% \text{ Cis} = \frac{A_{trans} - A_{cis}}{A_{trans}} \times 100$$

Where A_{trans} is the absorbance for the *trans* isomer at λ_{max} before light irradiation and A_{cis} is the absorbance for the *cis* isomer at the same wavelength measured at the photostationary state.[5-6]

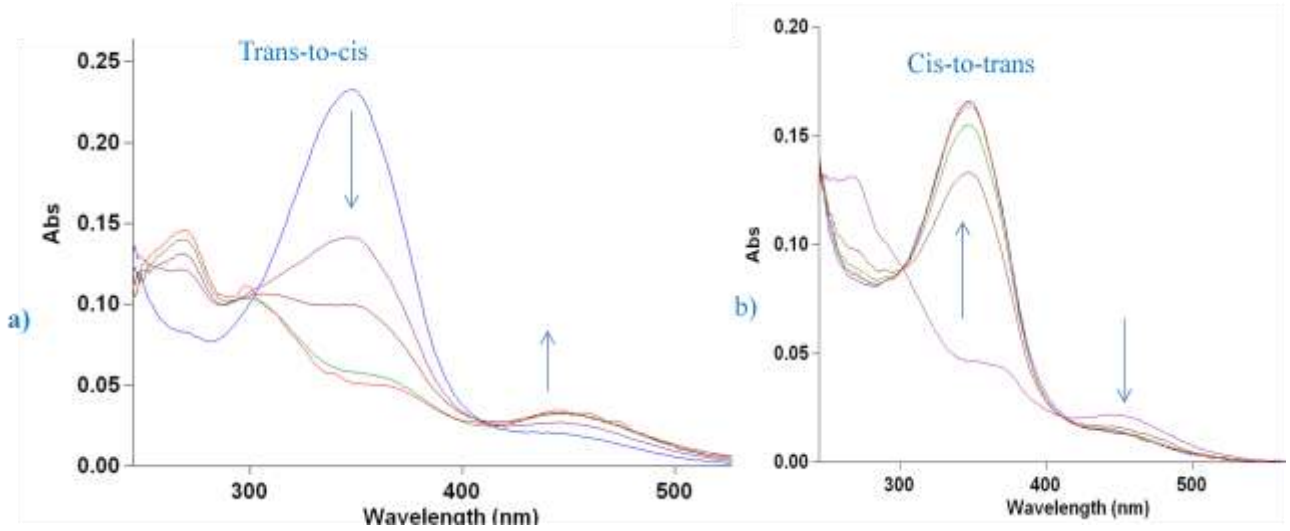


Fig. S17. UV-Vis spectra of **AzoPz-2**. a*) trans-to-cis* isomerization upon irradiation at λ = 365 nm at 0-80 seconds. b) *cis-to-trans* isomerization green light (λ = 530 nm) from 5-60 minutes.

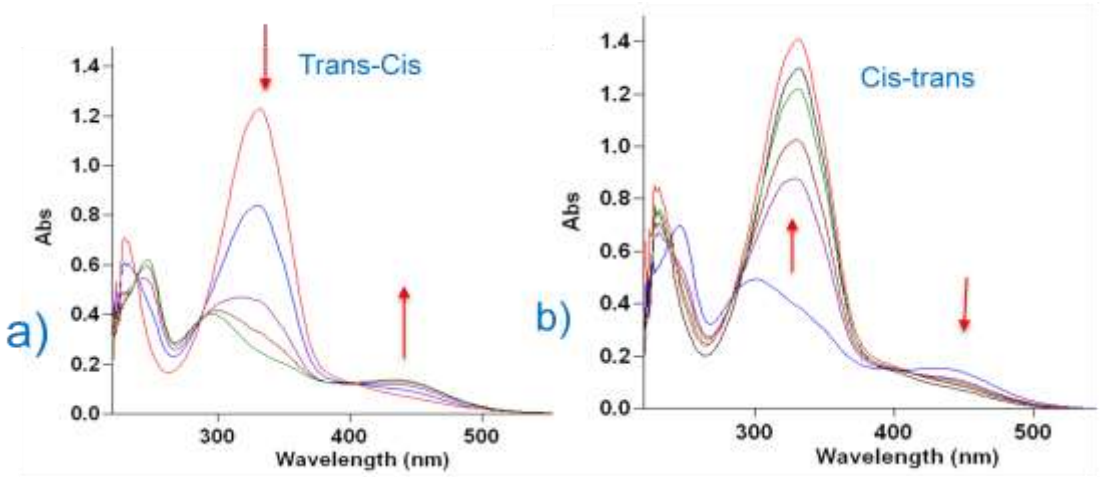


Fig. S18. UV-Vis spectra of **AzoPz-3**. a*) trans-to-cis* isomerization upon irradiation at λ = 365 nm at 0-120 seconds. b) *cis-to-trans* isomerization green light (λ = 530 nm) from 5-120 minutes.

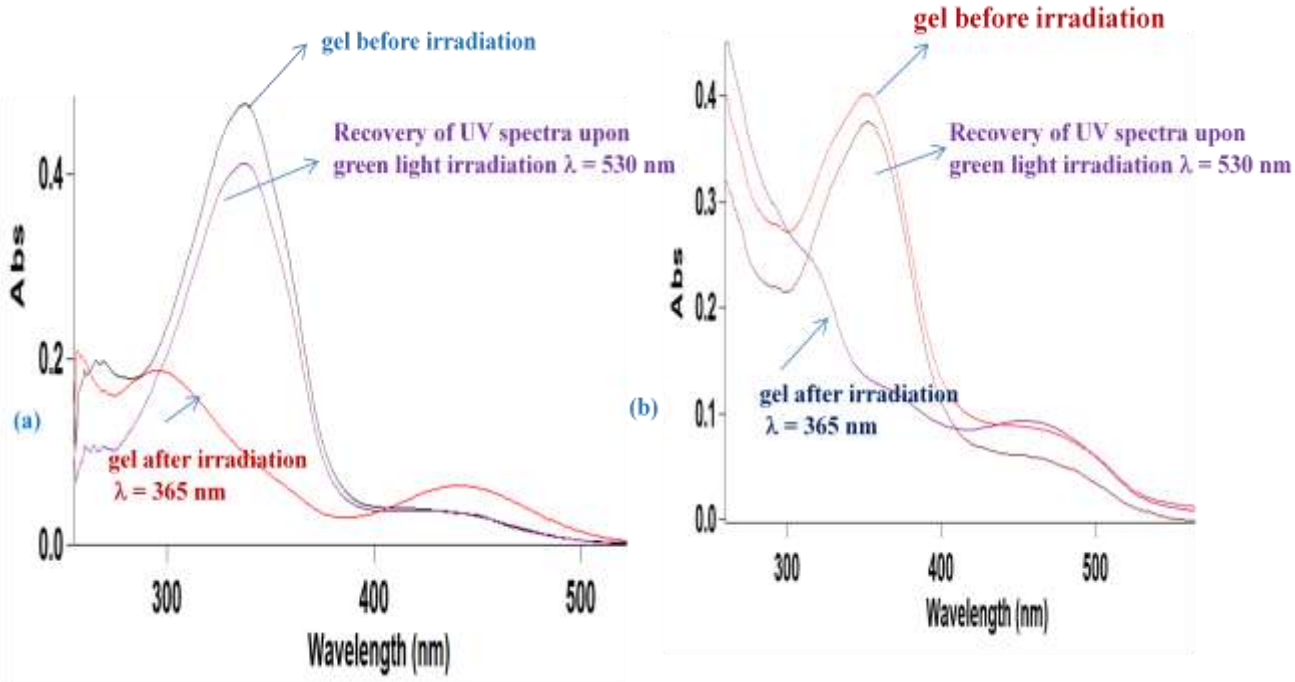


Fig. S19. Changes in the UV-vis spectrum of: (a) Zn-ImF-AzoPz-2 and (b) Zn-ImF-AzoPz-3 metallogel coassembly upon irradiation at λ = 365 nm and recovery of the spectrum upon irradiation with green light of λ = 530 nm.

Gel-sol photoswitching experiments. A 0.5 mg mL^{-1} metallogels of the trans forms of the metallogels was dissolved in DMSO and transferred to 1mm quartz cuvette. Then, the cuvette

was placed upside down and irradiated with 365 nm UV light, followed immediately by recording the absorption spectrum of the sol. The resulting solution was irradiated with green light or standing at RT to reform the gel.

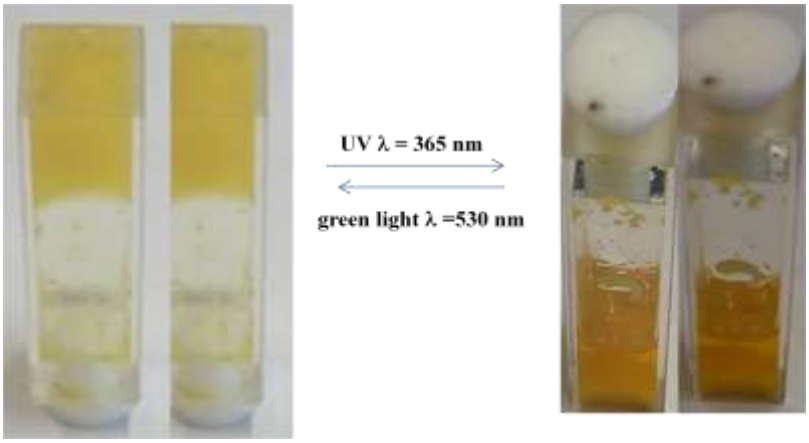
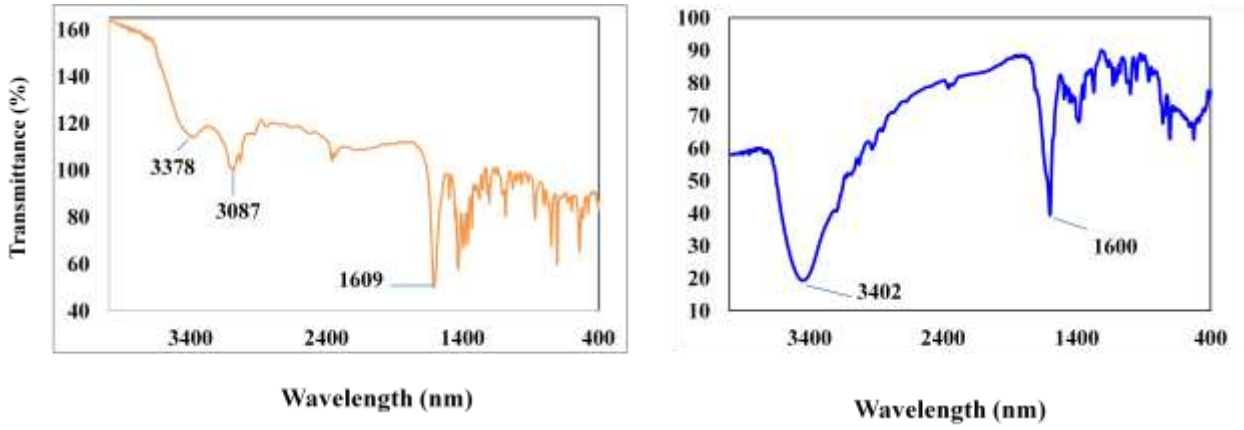


Fig. S20. Digital images of the Zn-ImF-AzOPz-2 and Zn-ImF-AzoPz-3 metallogel coassembly in a quartz cuvette before and after light irradiation showing partial gel dissolution.

6. FTIR spectra of ImF and metallogels

Fourier Transform Infrared (FTIR) spectra were recorded on a JASCO 4200 series spectrometer at room temperature. The samples for FTIR spectral measurements were prepared by using vacuum dried KBr pellets.



(a) **(b)**

Fig. S21. FTIR spectra of (**a**) ImF powder; (**b**) Zn-ImF-xerogel.

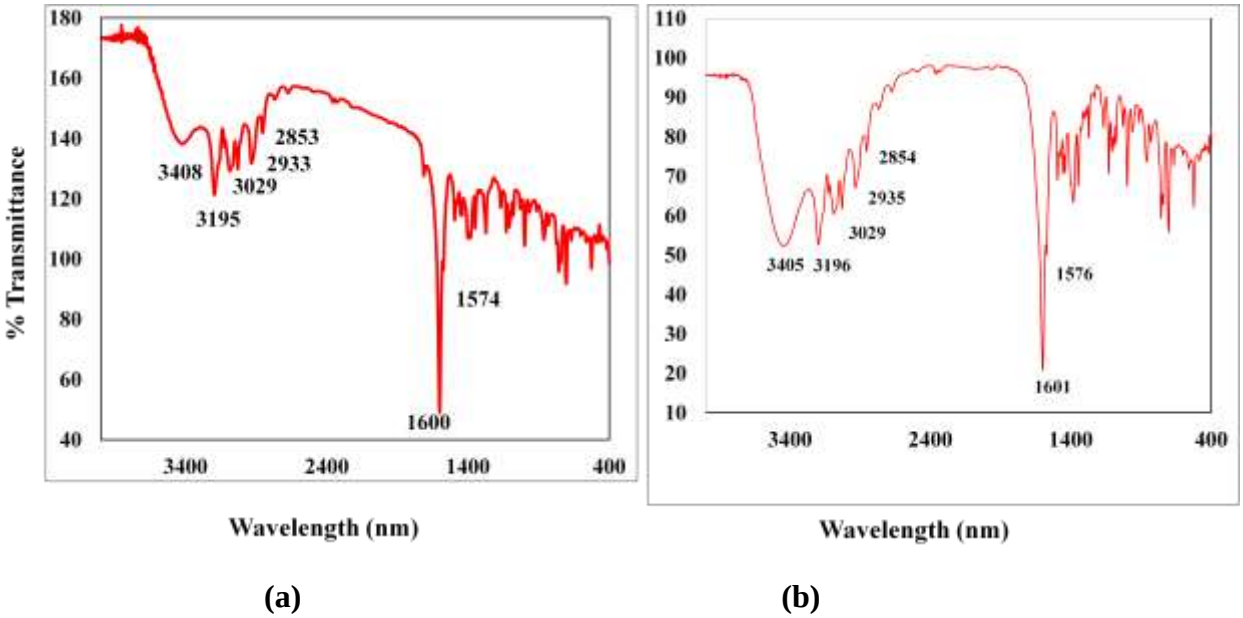


Fig. S22. FTIR spectra of (**a**) Zn-ImF-AzoPz-1; (**b**) Zn-ImF-AzoPz-2-xerogels.

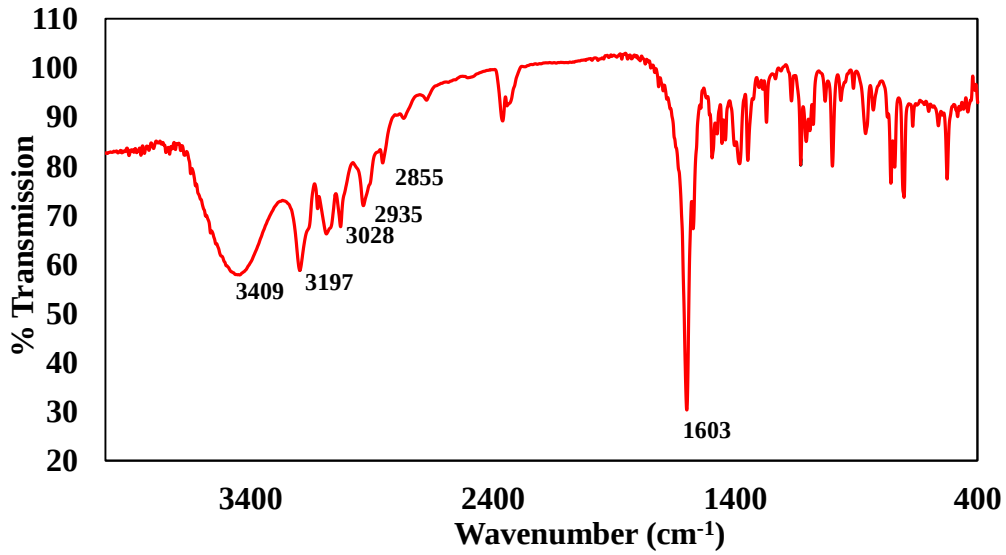


Fig. S23. FTIR spectra of Zn-ImF-AzoPz-3-xerogel.

6. Mass spectra (MS-ESI) of Zn-ImF metallogel

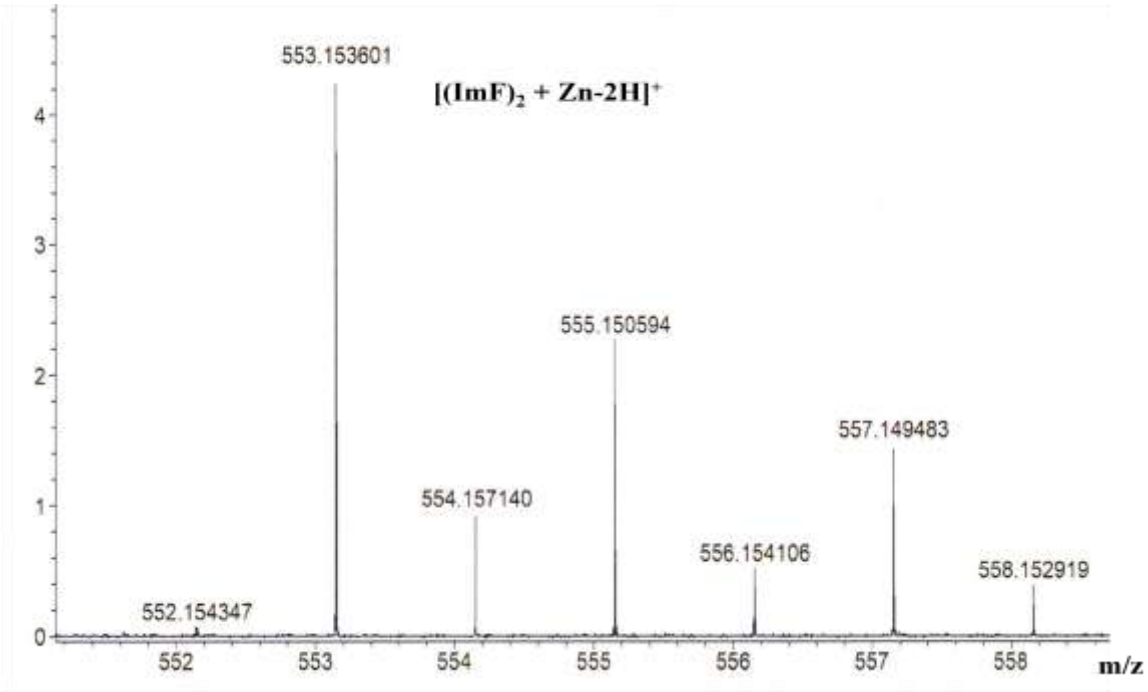


Fig. S24. Electrospray ionization mass spectra of Zn-ImF.

8. References

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