Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

A Photoactivatable Photochromic System Served as Self-Hidden Information Storage Material

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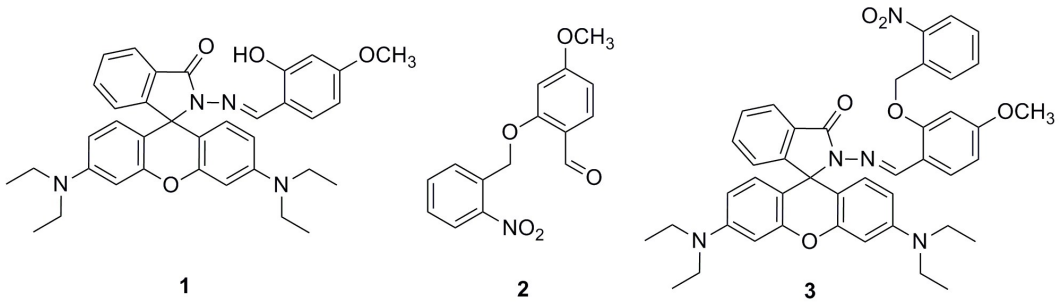
Materials and methods

All the materials of analytical grade were used in the experiment without further purification. Rhodamine B, hydrazine hydrate, 2-nitrobenzyl bromide, 2-hydroxy-4-methoxylbenzaldehyde, zinc nitrate hexahydrate and polyethylene glycol (PEG, average molecular weight 6000) were purchased from J&K Chemical Co., Beijing, China. All of the solvents were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China.

Absorption spectra were recorded by JASCO V-750 UV-Vis spectrophotometer. UV-Vis diffuse reflectance spectra were recorded by Agilent Cary 5000 UV-Vis-NIR Spectrometer, $BaSO_4$ plate was used as reference. NMR spectra were measured by JOEL JNM-ECA300 spectrometer operated at 300 MHz. ESI-MS spectra were obtained on Agilent Technologies 6420 triple quadrupole LC/MS without using the LC part. LD-T405F00 laser pointer was used to generate the laser of 405 nm and CNI GLP-450 laser was used to generate the laser of 450 nm in Video 1. The light sources used in Table 1 were produced by a CEL-HXF300/CEL-HXUV300 xenon light source with different optical filters (the half-peak width was about 15 nm). The light irradiation intensity was controlled as about 2 mW/cm^2. All the photos and videos were taken by a Canon EOS 600D camera with lens of EF-S 18-55mm IS II.

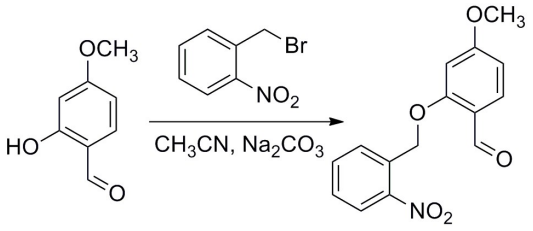
Synthesis



Scheme S1. Structures of the compounds **1**, **2** and **3**.

4-methoxylsalicylaldehyde rhodamine B hydrazone (1)

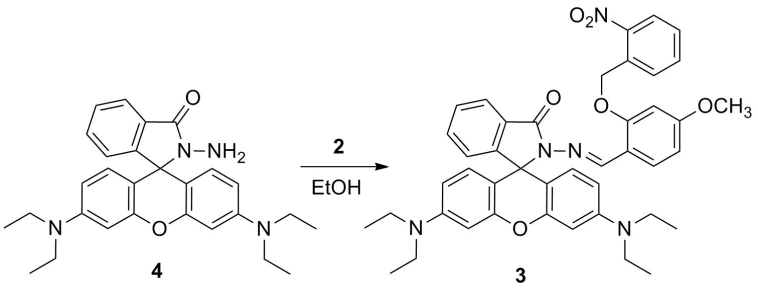
Compound **1** was prepared through our early reported procedure.[1]



Scheme S2. Synthetic route of **2**.

2-nitrobenzyloxyl-4-methoxylbenzaldehyde (2):

2-nitrobenzyl bromide (432 mg, 2 mmol) and 2-hydroxy-4-methoxylbenzaldehyde (304 mg, 2 mmol) were dissolved in 30 mL acetonitrile in a 100 mL flask. After being well mixed, sodium carbonate (316 mg, 2 mmol) was added. The mixture was stirred at room temperature overnight to yield a white precipitate. The precipitate was dissolved by the addition of 30 mL DCM. The mixture was washed with 50 mL water for three times and dried over $MgSO_4$. Then the solvent was removed under reduced pressure. 419 mg **2** (yield 73%) was obtained as white solid. ESI-MS spectrometry: *m/z* for $[M + H]^+$, calculated: 288.0866, found: 288.0867. ^{1}H NMR ($DCCl_3$) δ (ppm): 3.87 (s, 3H), 5.57 (s, 2H), 6.54 (d, 2H, J = 2.1 Hz), 6.61 (d, 1H, J = 8.6 Hz), 7.53 (t, 1H, J = 7.6 Hz), 7.74 (t, 1H, J = 7.2 Hz), 7.85 (d, 1H, J = 8.6 Hz), 7.97 (d, 1H, J = 7.6 Hz), 8.20 (d, 1H, J = 8.3 Hz), 10.40 (s, 1H). ^{13}C NMR ($DCCl_3$) δ (ppm): 55.83, 67.27, 99.44, 106.60, 119.39, 125.23, 128.48, 128.80, 131.72, 132.85, 134.42, 146.85, 161.84, 166.26, 187.90.



Scheme S2. Synthetic route of **3**

2-nitrobenzyloxyl-4-methoxylbenzaldehyde rhodamine B hydrazone (3):

Rhodamine B hydrazide (**4**) was prepared through an early reported procedure.[2] To a 100 mL flask, **4** (457 mg, 1 mmol) and **2** (287 mg, 1 mmol) were dissolved in 30 mL absolute ethanol. The mixture was stirred and heated to reflux overnight. Then the solvent was concentrated to about 15 mL under reduced pressure. After being cooled to 4 ^{o}C, white precipitate was obtained. The precipitate was washed with 20 mL cold absolute ethanol for three times. 442 mg **3** (yield 61%) was obtained as white solid. MS-ESI spectrometry: *m/z* for $[M + H]^+$, calculated: 726.3286, found: 726.3284. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.00 (t, 12H, J = 6.9 Hz), 3.22 (m, 8H), 3.70 (s, 3H), 5.44 (s, 2H), 6.32 (m, 4H), 6.45 (d, 2H, J = 9.5 Hz), 6.58 (m, 2H), 7.04 (d, 1H, J = 6.9 Hz), 7.53 (m, 3H), 7.66 (m, 2H), 7.88 (m, 2H), 8.20 (d, 1H, J = 7.9 Hz), 8.90 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 12.84, 44.13, 55.95, 65.51, 67.17, 97.95, 100.34, 105.93, 107.61, 108.56, 116.70, 123.44, 124.02, 125.39, 126.94, 127.87, 128.81, 128.93, 129.09, 129.42, 133.07, 134.12, 134.74, 142.30, 147.51, 148.95, 152.26, 152.97, 157.96, 162.82, 164.23.

Selected spectra and data referred in the paper

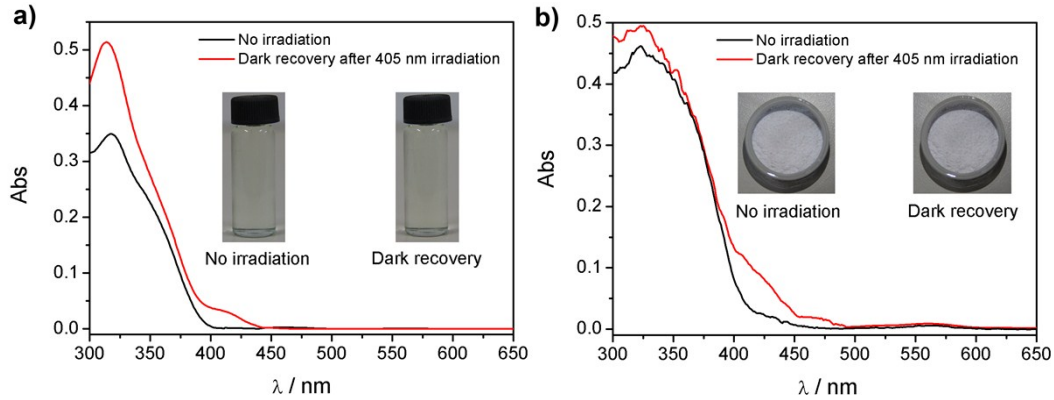


Figure S1. Absorbance spectra and photographs of unirradiated **3-Zn** and dark-recovered **3-Zn** (after 405 nm irradiation) in a) THF and b) PEG. Conditions: for a) [**3**] = 10 μmol/L, [Zn(II)] = 100 μmol/L, For b) [**3**] = 1 μmol/g, [Zn(II)] = 10 μmol/g.

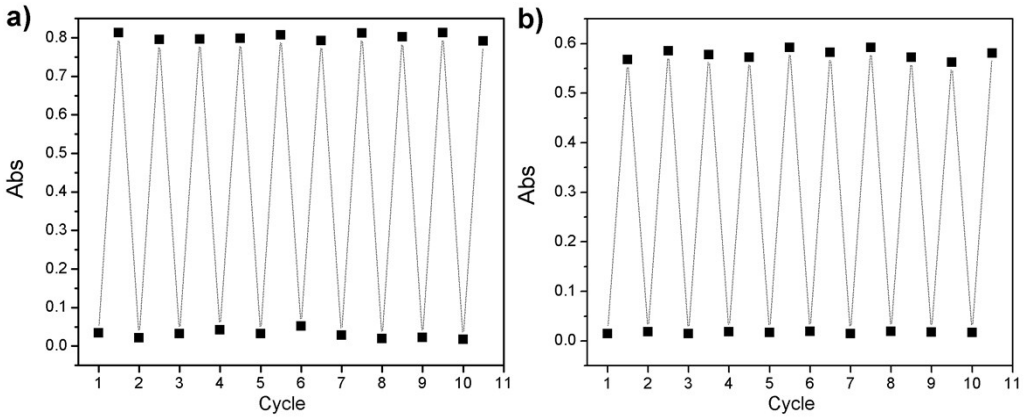


Figure S2. Fatigue resistance of **1-Zn** in a) THF and b) PEG (λ = 554 nm) upon 405 nm light irradiation and stand in dark alternatively.

Caption of videos

Video 1: A video of information storage on **3-Zn** in PEG. [**3**] = 1 μmol/g, [Zn(II)] = 10 μmol/g.

References

[1] K. Li, Y Xiang, A. J. Tong, B. Z. Tang, *Sci China Chem*, **2014**, *57*, 248-251

[2] Y. Xiang, A. J. Tong, P. Y. Jin,Y. Ju, *Org Lett*, **2006**, *8*, 2863-2866

NMR spectra

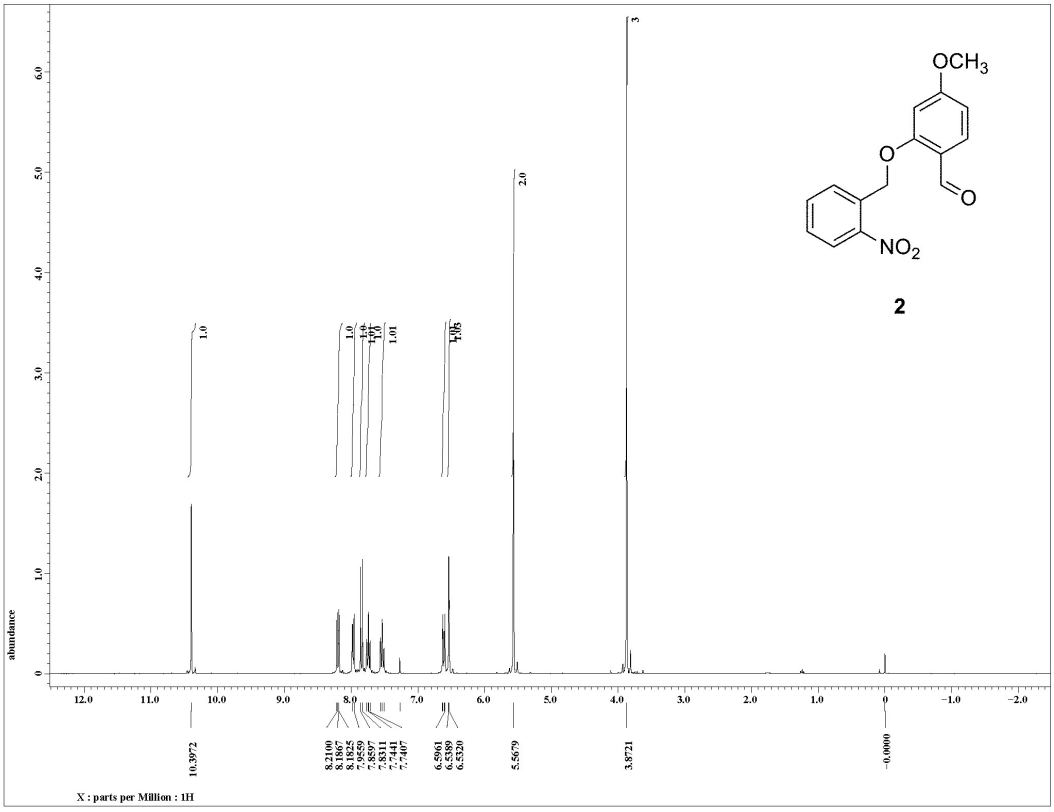


Figure S3. ^{1}H-NMR spectrum of **2** in $DCCl_3$.

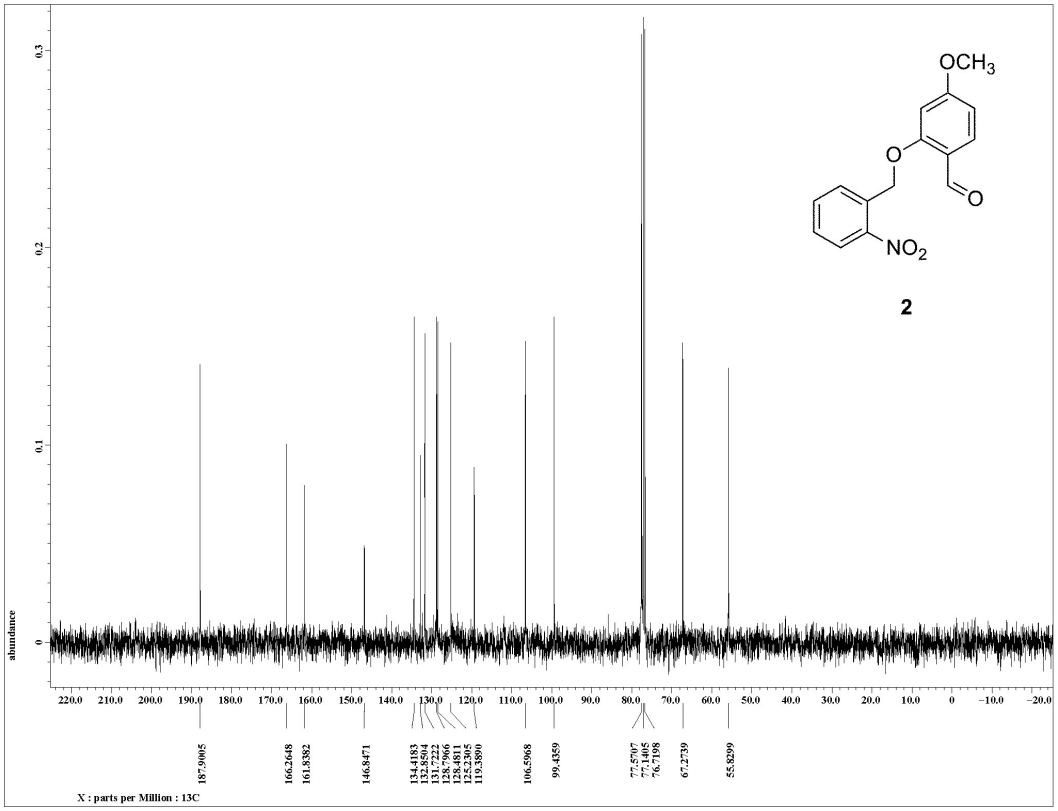


Figure S4. ^{13}C-NMR spectrum of **2** in $DCCl_3$.

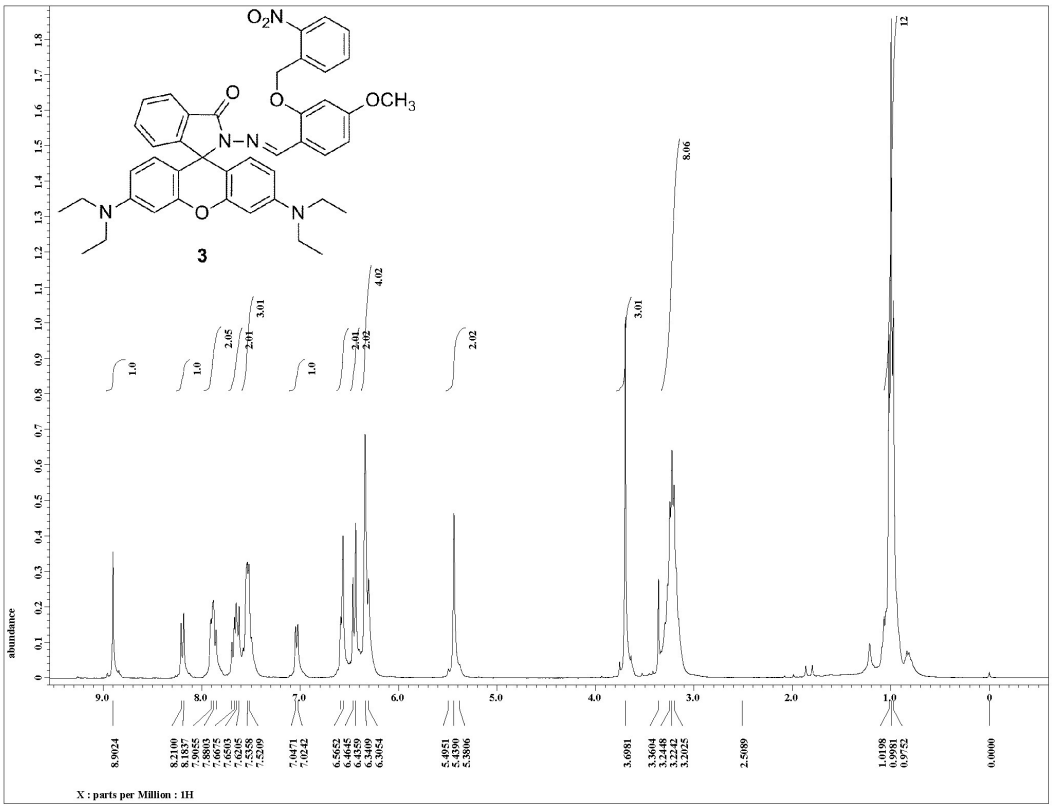


Figure S5. ^{1}H-NMR spectrum of **3** in DMSO-d_6.

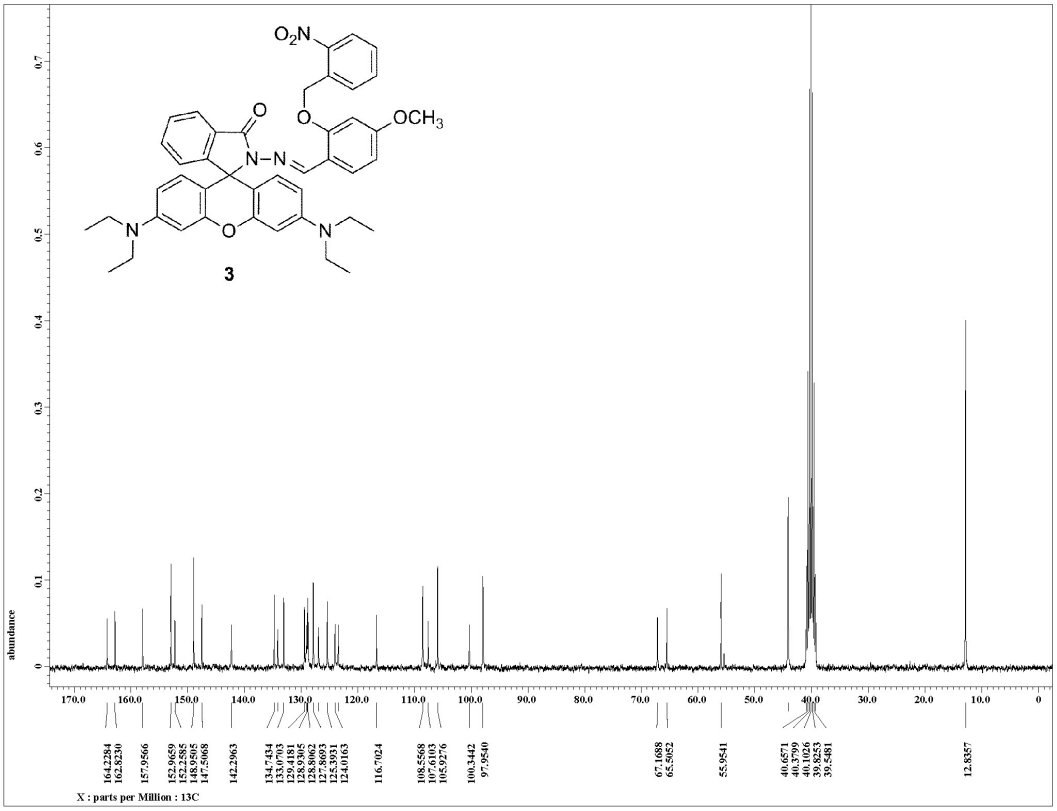


Figure S6. ^{13}C-NMR spectrum of **3** in DMSO-d_6.

ESI-MS spectra

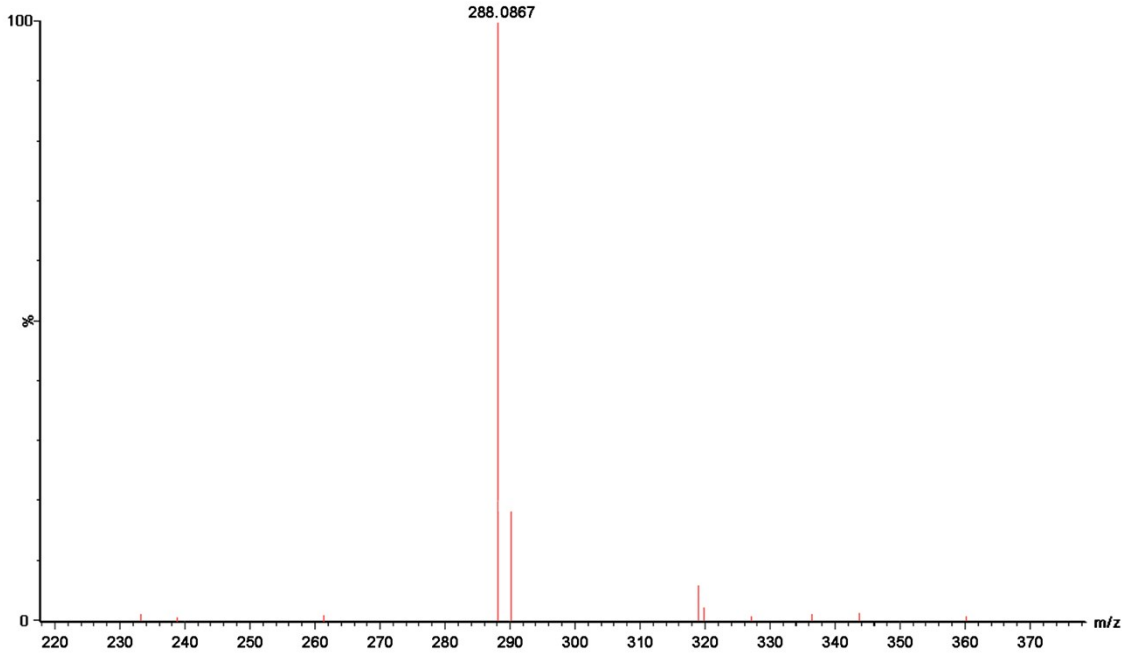


Figure S7. ESI-MS spectrum of **2**.

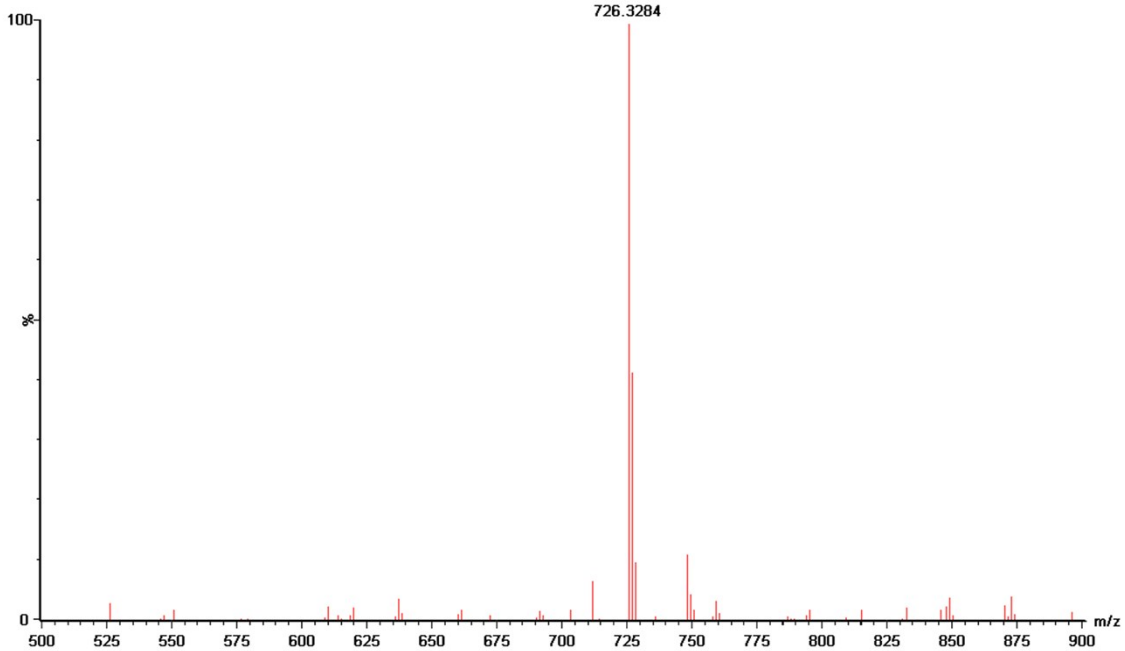


Figure S8. ESI-MS spectrum of **3**.