

Supporting Information

Novel triphenylamine functionalized bithiazole-metal complex with C₆₀ for photocatalytic hydrogen production under visible light irradiation

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Experimental section

Materials

All the reagents and solvents were analytical grade and used directly without any purification. Among them, rubenic acid (99.0%) was purchased from TCI (Tokyo Chemical Industry Co., Ltd.). Iodomethane (CH₃I, AR), ethanol (AN, analytical grade) and acetic acid (HAc, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Copper(II) bromide (CuBr₂, 99%), 2'-hydroxyacetophenone (99%), *N*-bromosuccinimide (NBS, 99%), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄, Pd ≥ 9.0%), boron tribromide (BBr₃, 99.9%), copper(II) chloride (CuCl₂, 98%), cobalt(II) chloride (CoCl₂, 99.7%), lithium chloride (LiCl, 99.998%), fullerene (C₆₀, 99.9%), sodium sulfate anhydrous (Na₂SO₄, 99.99%) and sodium carbonate anhydrous (Na₂CO₃, 99.99%) was purchased from Aladdin Co. Ltd. 4-(Diphenylamino)phenylboronic acid (TPA, 98%) was purchased from Ruiyuan Group Limited (Yurui Chemical Co., Ltd.). Meanwhile, Nafion (5%), ruthenium chloride anhydrous (RuCl₃, 99.99%) and commercial TiO₂ (P25) was purchased from J&K Chemical Ltd. Laboratory deionized (DI) water was achieved from an ultrapure water system, resulting in a resistivity >18 MΩ cm.

Instruments

All the melting points were determined on a Yuhua X4 melting point apparatus (Gongyi, China) and were uncorrected. Infrared (IR) spectra were recorded on a Bruke Tensor 27 Fourier transform infrared (FT-IR) spectrometer by the KBr salt slice method in the absorption range of 4000-400 cm⁻¹. ¹H and ¹³C NMR spectra were obtained in DMSO-*d*₆ on a Bruker DRX-400 MHz spectrometer and tetramethylsilane (TMS) was used as internal standard. The mass spectra (MS) were recorded on

Thermo LCQ DECA XP MAX mass spectrometer. Elemental analysis was performed on a Perkin Elmer Series II 2400 elemental analyzer.

UV-visible (UV-vis) spectra was measured by Hitachi U-3010 absorption spectrophotometer. Photoluminescence (PL) spectrum was obtained on a Hitachi F-4500 fluorescence spectrophotometer at room temperature, using $\lambda_{\text{ex}} = 410 \pm 5$ nm. And the solid fluorescence quantum yields (ϕ_{PL}) values were determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 415$ nm).¹

The crystallinity of as-prepared samples were characterized by Bruker D8 Advance X-ray diffractometer (XRD, Bruker, Germany) with Cu K_{α} radiation ($\lambda = 0.15406$ nm). The diffraction patterns were measured over the 2θ angle range from 10° to 80° with a scanning rate of $8^{\circ} \cdot \text{min}^{-1}$ and a step size of 0.01° .

The transmission electron microscope (TEM) was used to investigate the crystallographic structures and HR-TEM modes at different scales (TecnaiG220, FEI). The composition of sample was characterized by energy dispersive X-ray spectroscopy (EDS, JEM-2100).

X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) measurements were carried out with an monochromatic X-ray source (Al K_{α} , 15 kV, 200 W).

Raman spectra were measured by micro-Raman spectrometer (Renishaw InVia) in the backscattering geometry using an Ar ion laser (514.5nm) as an excitation source at room temperature.

The Brunauer-Emmett-Teller (BET) specific surface area of samples was evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a Quantochrome NOVA 1200e instrument.

Time-resolved decay curves were measured by Edinburgh FLS 920 Fluorescence spectrometer.

The photocurrents and electrochemical impedance spectroscopy (EIS) were carried out by using an electrochemical analyzer (CHI660C Instruments, Shanghai, China) with a standard three-electrode system. The as-prepared sample was used as working electrode, a platinum wire was employed as a counter electrode and Ag/AgCl (saturates KCl) as a reference electrode, respectively. The supporting

electrolyte was 10% (v/v) lactic acid mixed with Na₂SO₄ (0.5 mol•L⁻¹) aqueous solution. Indiumtin oxide (ITO, 2 × 1 cm²) with a thickness of 188 nm on a glass substrate were successively cleaned using acetone, methanol, isopropanol, and DI water in a sonicator, each for 30 min. The working electrodes were prepared as follows: 0.05 g of the as-synthesized photocatalysts **4-6** and P25 was separately ground with 20 μL of a Nafion (5%) aqueous solution and 100 μL of ethanol to make slurry. The slurry was then coated onto ITO glass electrodes with an active area of 1.0 cm², and these electrolytes were dried at 120°C for 1 h in a flowing nitrogen atmosphere. All the investigated electrodes have the same film thickness of 15 μm. The photocurrent densities produced at a bias of 0.5 V versus Ag/AgCl under light irradiation of 420 nm (light on/off cycles: 50 s), and the stability of the materials were conducted under the same condition (light on). EIS was determined at the bias of the open circuit voltage (VOC), and recorded over the frequency range of 0.1-10⁵ Hz with an ac amplitude of 10 mV.

Synthetic procedures of the compounds IV, V and 2TPABTz

Syntheses of compounds I -III were reported in the literature.^{2,3}

Preparation of Compound IV⁴

Compound III (6.00 mmol) and NBS (12.2 mmol) were dissolved in a mixture of acetic acid (20 mL) and *N,N*-dimethylformamide (DMF, 20 mL). After stirring overnight in the dark, a solid was precipitated in the reaction mixture. The precipitate was filtered, washed with methanol, and then purified by column chromatography (silica gel, cyclohexane-CH₂Cl₂) to afford compound IV.

Preparation of Compound V⁵

THF (20 mL) and an aqueous solution of K₂CO₃ (2.0 M, 10 mL) were added to a round bottom flask containing compound IV (1 mmol), the heteroarylboric acid (2.2 mmol) and Pd(PPh₃)₄ (0.2 mmol)

under nitrogen. The mixture was heated to reflux and monitored by TLC. When the reaction was completed (about 12 h), the products were extracted with CH_2Cl_2 . The combined organic layers were dried with anhydrous NaSO_4 , and concentrated under vacuum to give crude products, which was purified by column chromatography on silica gel with gradient eluent of the mixtures of cyclohexane and ethyl acetate to afford the desired compound **V**.

Preparation of Compound **2TPABTz**³

A solution of BBr_3 (2 mmol) in dry CH_2Cl_2 (15 mL) was slowly added to a solution of **V** (0.5 mmol) in dry CH_2Cl_2 (15 mL) at room temperature for 3 h. The aqueous layer was extracted with CH_2Cl_2 washed with brine and dried over anhydrous Na_2SO_4 , and then evaporated to give **2TPABTz**.

Preparation of different kinds of photocatalysts^{6,7}

Synthesis of the complex **1**

To a solution of CuCl_2 (0.0134 g, 0.1 mmol) in methanol (5 mL) was added dropwise a solution of compound **2TPABTz** (0.0839 g, 0.1 mmol) in methanol (10 mL) for a period of 20 minutes. The resulting mixture was slowly heated to 100°C and maintained at this temperature for 6 hours. Afterward, diethyl ether (15 mL) were added to induce the precipitation of a solid. Then it was filtered and washed with diethyl ether ($10\text{ mL} \times 3$) and recrystallized from chloroform to obtain a light-red solid.

Synthesis of the complex **2**

Similarly, a mixture of CoCl_2 (0.0130 g, 0.1 mmol) and methanol (5 mL) were stirred at room temperature, then compound **2TPABTz** (0.0839 g, 0.1 mmol) and methanol (10 mL) were added with continuous stirring in 20 minutes. The resulting cloudy solution was gradually heated to 100°C , and held at that temperature for 6 hrs. Subsequently, addition of diethyl ether (15 mL) induced precipitation of a solid that was filtered and washed extensively with diethyl ether ($10\text{ mL} \times 3$) to yield a brown solid.

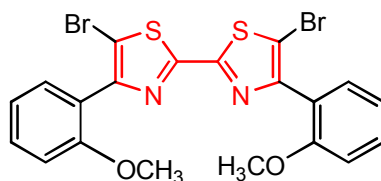
Synthesis of the complex **3**

RuCl₃ (0.0207 g, 0.1 mmol), Compound **2TPABTz** (0.0839 g, 0.1 mmol), and LiCl (0.0021 g, 0.05 mmol) were dissolved in DMF (20 mL). The reaction was heated at 100 °C in an oil bath and refluxed for 6 h. After that, the mixture was cooled to room temperature, acetone (50 mL) was added and the resultant solution cooled at 0 °C overnight. The precipitate was collected by vacuum filtration, washed with DI water and diethyl ether three times. And then the residue was dried under vacuum to obtain the black solid.

Typical procedure for the synthesis of composites **4-6**⁸⁻¹⁰

An appropriate amount of C₆₀ was added to 30 mL toluene and sonicated for 1 h to make C₆₀ disperse totally. The as-synthesized complex **1-3** was added to the above solution and continuous stirring for 6 h at room temperature, respectively. After volatilization of the toluene, the resulting powder was washed with ethanol and DI water for three times, and dried under vacuum at 60 °C for 12 h to obtain the C₆₀ hybridized complex samples. Besides, the composite **6** with different mass ratios of C₆₀ (from 0.5 to 10.0 wt%) were prepared by following the same procedure as above.

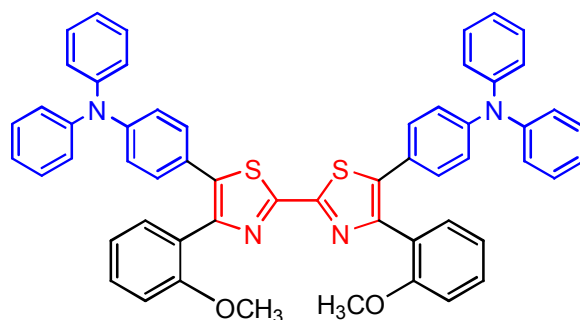
5,5'-dibromo-4,4'-bis(2-methoxyphenyl)-2,2'-bithiazole (IV)



White powder, yield 77%; m.p. 208.7-210.4 °C; UV-vis (CH₂Cl₂) λ_{max}: 272 nm; ¹H NMR (400 MHz, DMSO-TMS, ppm) δ: 3.92 (s, 6H, CH₃), 6.95-7.07 (m, 4H, ArH), 7.25-7.29 (m, 2H, ArH), 8.32 (d, J =

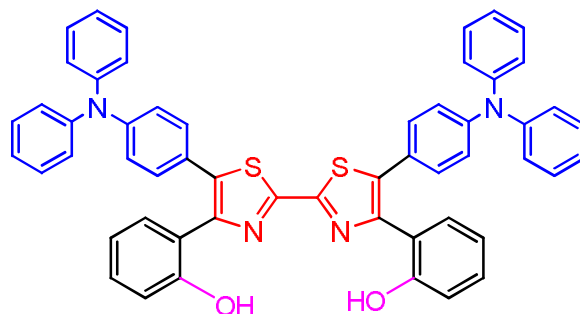
8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-TMS, ppm) δ : 56.11, 98.27, 111.67, 118.30, 121.47, 129.86, 131.02, 157.12, 161.12, 165.30; IR (film, cm^{-1}) ν : 3066, 3053, 3036, 1695, 1678, 1596, 1578, 1484, 1370, 1251, 1187, 1088, 1023, 976, 755, 721, 663; ESI-MS, m/z (%): 561 ($[\text{M}+\text{Na}]^+$, 100); Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2$: C 44.59, H 2.60, N 5.20, S 11.89; Found: C 44.66, H 2.65, N 5.14, S 11.82.

4,4'-(4,4'-bis(2-methoxyphenyl)-2,2'-bithiazole-5,5'-diyl)bis(N,N-diphenylaniline) (V)



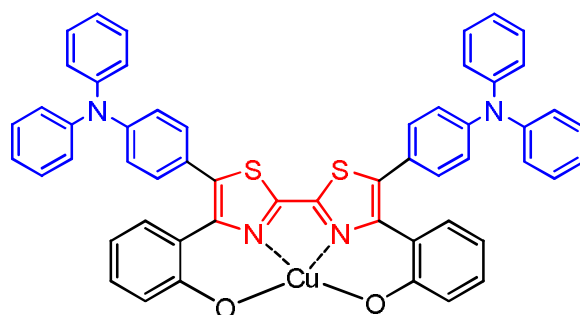
Pale green solid, yield 82%; m.p. 237.2-238.5 °C; UV-vis (CH_2Cl_2) λ_{max} : 288 nm; ^1H NMR (400 MHz, DMSO-TMS, ppm) δ : 3.77 (s, 6H, 2 CH_3), 7.06-7.15 (m, 20H, ArH), 7.17-7.21 (m, 4H, ArH), 7.27-7.37 (dd, $J_1 = J_2 = 8.0$ Hz, 8H, ArH), 7.60 (d, $J = 8.0$ Hz, 2H, ArH), 8.28 (d, $J = 8.0$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-TMS, ppm) δ : 57.86, 117.25, 119.75, 121.01, 123.80, 125.44, 126.63, 128.40, 128.87, 129.40, 130.19, 130.88, 131.28, 147.18, 148.01, 158.67, 159.43, 160.27; IR (film, cm^{-1}) ν : 3083, 3058, 3029, 1657, 1594, 1584, 1549, 1493, 1344, 1246, 1188, 1075, 1027, 972, 753, 694; ESI-MS, m/z (%): 889 ($[\text{M}+\text{Na}]^+$, 100); Anal. Calcd for $\text{C}_{56}\text{H}_{42}\text{N}_4\text{O}_2\text{S}_2$: C 77.50, H 4.84, N 6.46, S 7.38; Found: C 77.47, H 4.92, N 6.57, S 7.25.

2,2'-(5,5'-bis(4-(diphenylamino)phenyl)-2,2'-bithiazole-4,4'-diyl)diphenol (2TPABTz)



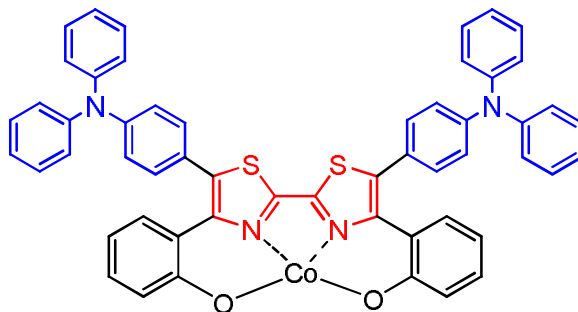
Yellow solid, yield 35%; m.p. 225.7-227.3 °C; UV-vis (CH₂Cl₂) λ_{max}: 302 nm; ¹H NMR (400 MHz, DMSO-TMS, ppm) δ: 7.00-7.12 (m, 8H, ArH), 7.28-7.37 (m, 6H, ArH), 7.44-7.58 (m, 8H, ArH), 7.59-7.65 (m, 8H, ArH), 7.82 (d, *J* = 8.0 Hz, 4H, ArH), 8.25 (d, *J* = 8.0 Hz, 2H, ArH), 10.33 (s, 2H, 2OH); ¹³C NMR (100 MHz, DMSO-TMS, ppm) δ: 118.28, 119.61, 121.18, 123.68, 124.25, 126.15, 127.89, 128.67, 128.79, 129.47, 129.60, 130.26, 146.90, 156.34, 157.34, 159.20; IR (film, cm⁻¹) ν: 3442, 3055, 3034, 2998, 2964, 2817, 1631, 1518, 1360, 1076, 783, 758; ESI-MS, *m/z* (%): 861 ([M+Na]⁺, 100); Anal. Calcd for C₅₄H₃₈N₄O₂S₂: C 77.23, H 4.53 N 6.67, S 7.63; Found: C 77.31, H 4.45, N 6.58, S 7.71.

the copper complex (1)



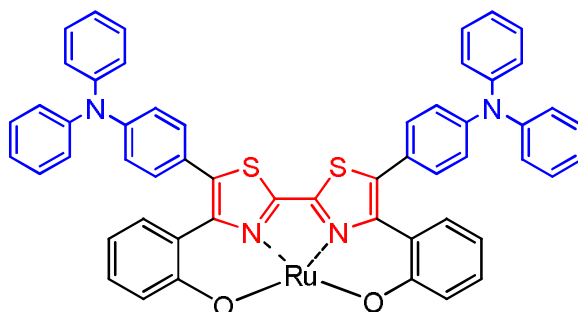
Light-red solid, yield 63%; m.p. 269.5-271.2 °C; ESI-MS, *m/z* (%): 900 ([M+H]⁺, 100); IR (film, cm⁻¹) ν: 3060, 3027, 2944, 2871, 1602, 1516, 541, 413; Anal. Calcd for C₅₄H₃₆CuN₄O₂S₂: C 71.95, H 4.00 N 6.22, S 7.11; Found: C 71.99, H 4.11, N 6.08, S 7.17.

the cobalt complex (2)



Brown solid, yield 49%; m.p. 285.2-286.4 °C; ESI-MS, m/z (%): 896 ($[M+H]^+$, 100); IR (film, cm^{-1}) ν : 3052, 3018, 2957, 2893, 1624, 1538, 562; Anal. Calcd for $\text{C}_{54}\text{H}_{36}\text{CoN}_4\text{O}_2\text{S}_2$: C 72.33, H 4.02 N 6.25, S 7.14; Found: C 72.29, H 4.07, N 6.18, S 7.21.

the ruthenium complex (3)



Black solid, yield 27%; m.p. 299.7-301.1 °C; ESI-MS, m/z (%): 939 ($[M+H]^+$, 100); IR (film, cm^{-1}) ν : 3044, 3029, 2911, 2855, 1613, 1520, 637; Anal. Calcd for $\text{C}_{54}\text{H}_{36}\text{RuN}_4\text{O}_2\text{S}_2$: C 69.08, H 3.84 N 5.97, S 6.82; Found: C 69.02, H 3.92, N 6.02, S 6.88.

Table S1. Surface element composition of composite **6** as detected with XPS before (a) and after (b) the recycling photocatalytic experiments

Sample	Element concentration (atom%)				
	C 1s	O 1s	Ru 3p	N 1s	S 2p
a	79.91	2.02	9.64	4.07	4.36
b	80.11	1.87	9.51	4.34	4.17

Photocatalytic hydrogen production¹¹⁻¹³

Photocatalytic experiments for hydrogen (H₂) evolution were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. In a typical photocatalytic experiment, 0.05 g of the target photocatalyst was suspended in a mixed solution of lactic acid (10 mL) and water (90 mL) for H₂ production. A high-pressure Xe lamp (300 W) was used as the light source to trigger the photocatalytic reactions, which was positioned on the side of photoreactor. The as-prepared sample was continuously suspended in the aqueous solution with a magnetic stirrer during the irradiation. The temperature of the reactant solution was maintained at 25 °C by the recirculation cooling water during the reaction. Prior to illumination, the suspension was thoroughly degassed for 1 h by nitrogen gas purging. The amount of H₂ generated was analyzed by online gas chromatography (GC7900, Tian Mei, Shanghai), using a 5 Å molecular sieve column with a thermal conductivity detector (TCD).

Determination of QE values^{12, 13}

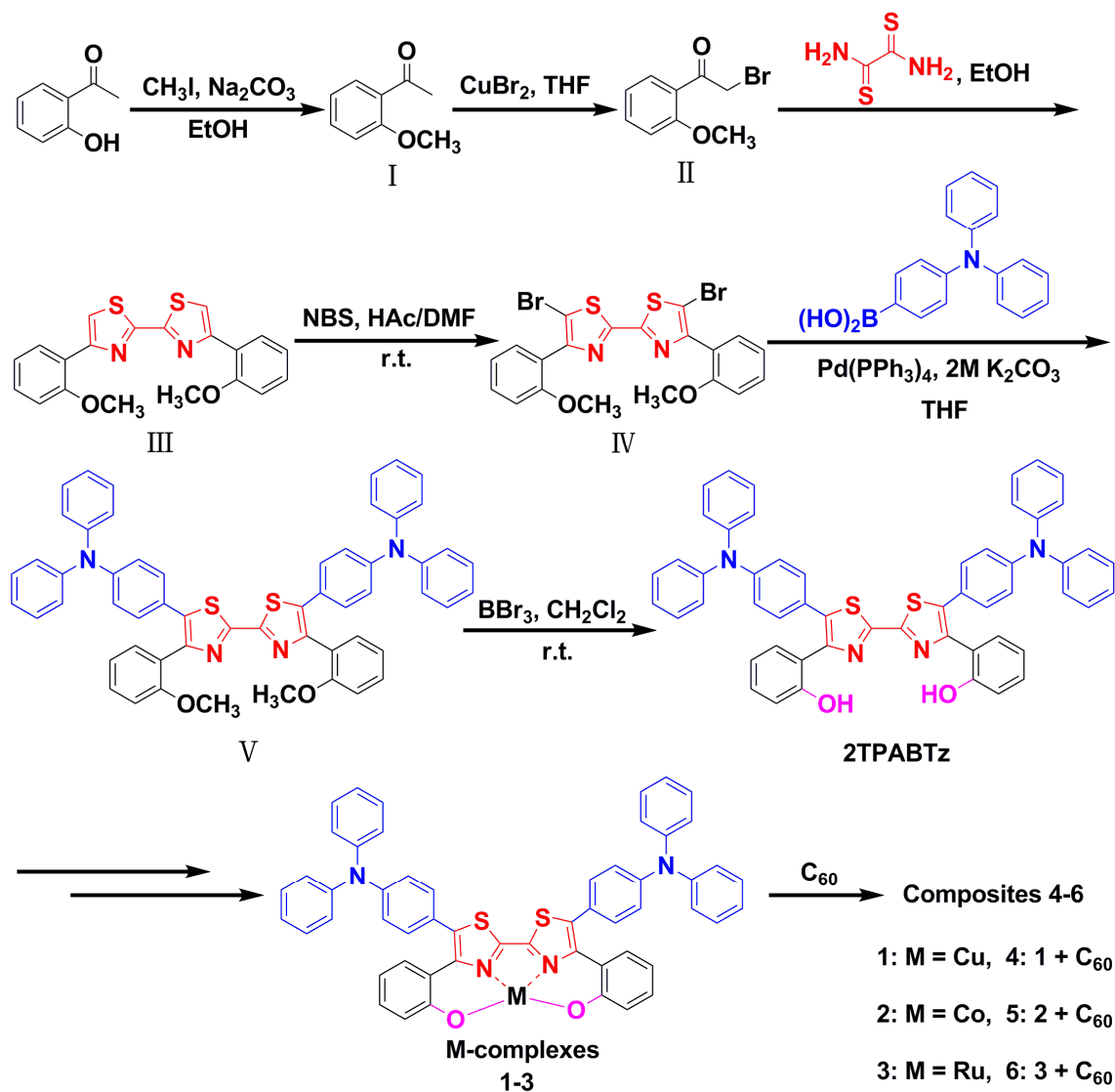
Apparent quantum efficiency (QE) was measured under identical photoreaction conditions except for the incident mono-chromatic light with a band-pass filter ($\lambda = 420$ nm, half width = 15 nm) and an irradiatometer. The hydrogen yields of 1 h photocatalytic reaction were measured in one continuous reaction under visible light with the wavelength of 420 nm. The incident photon number was obtained on a calibrated Si photodiode (SRC-1000-TC-QZ-N, Oriel), and the QE value was defined by the following equation.

$$\text{QE}\% = \frac{2 \times \text{Number of evolved H}_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\%$$

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Scheme S1. Synthesis of triphenylamine functionalized bithiazole (2TPABTz)-based M complexes and the corresponding composites 1-6

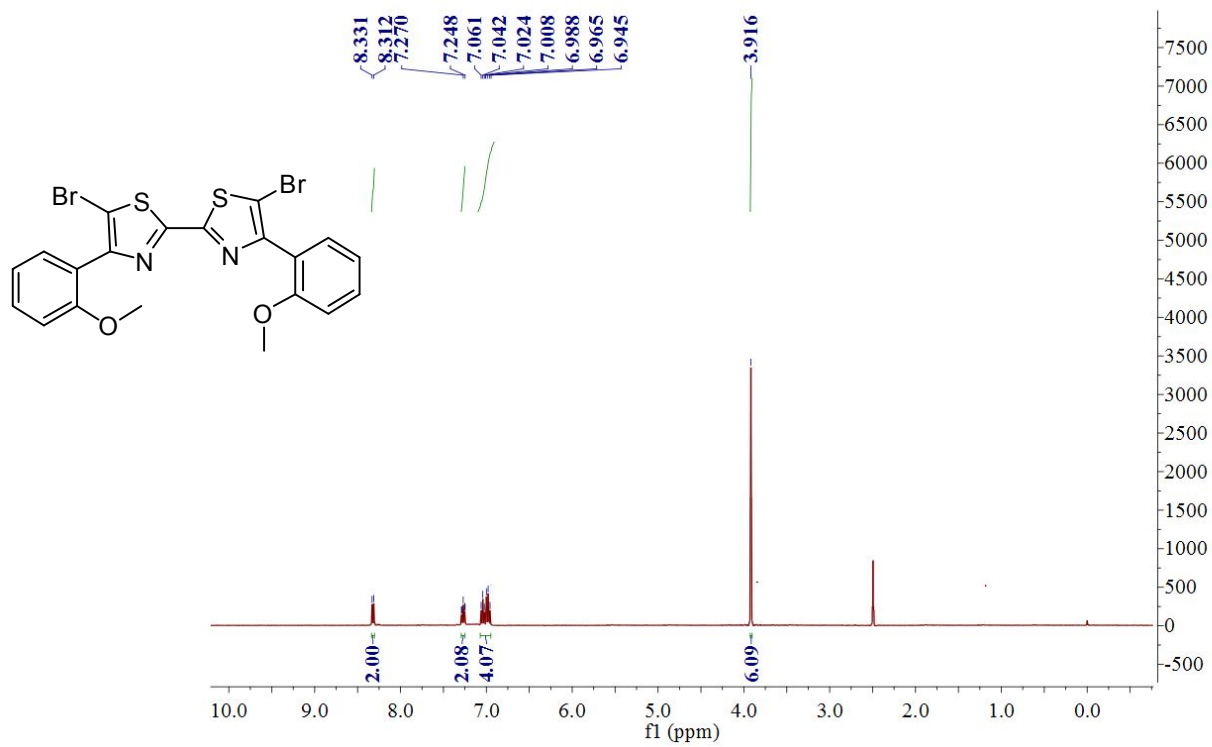


Figure S1. ¹H NMR spectrum of the compound IV

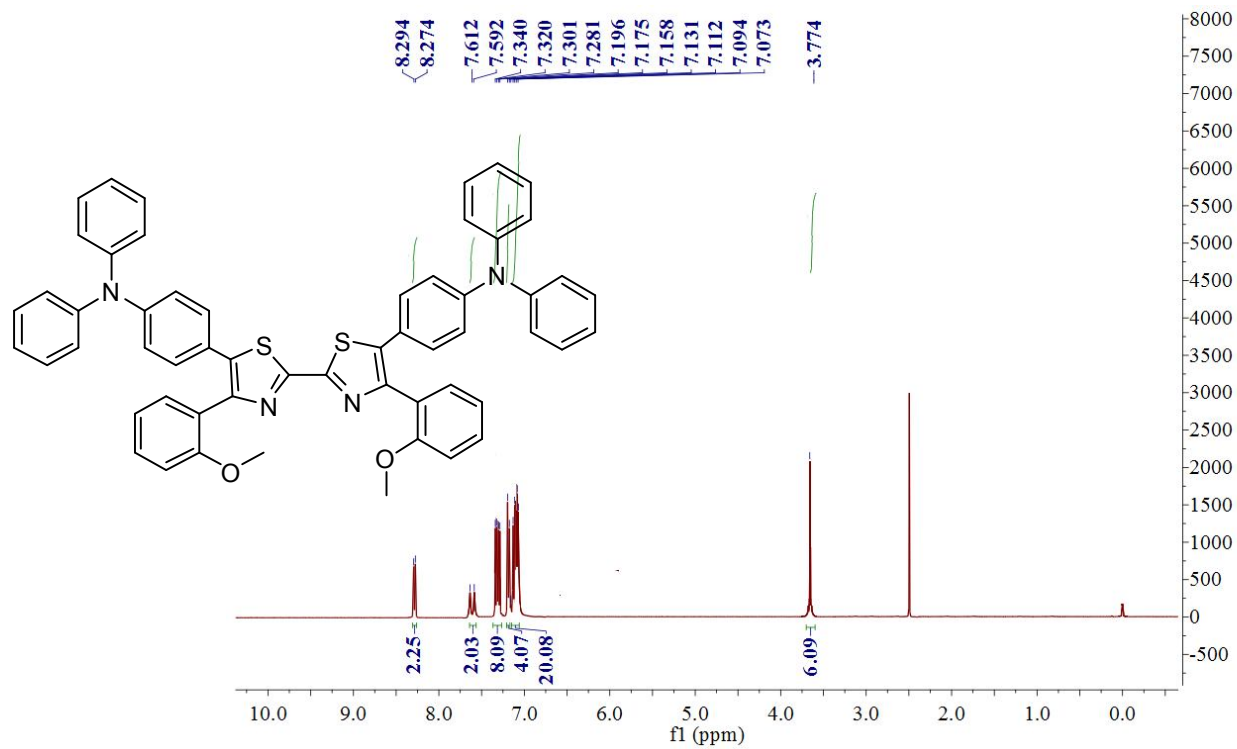


Figure S2. ¹H NMR spectrum of the compound V

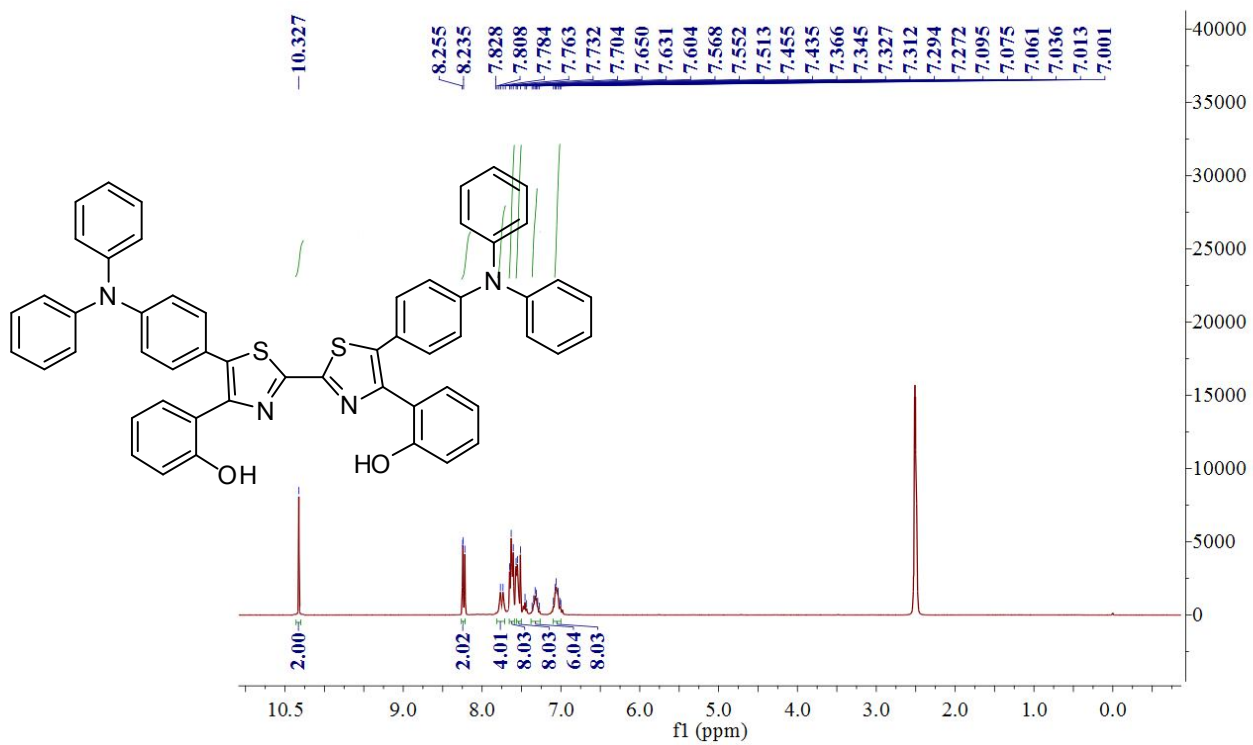


Figure S3. ¹H NMR spectrum of the compound 2TPABTz

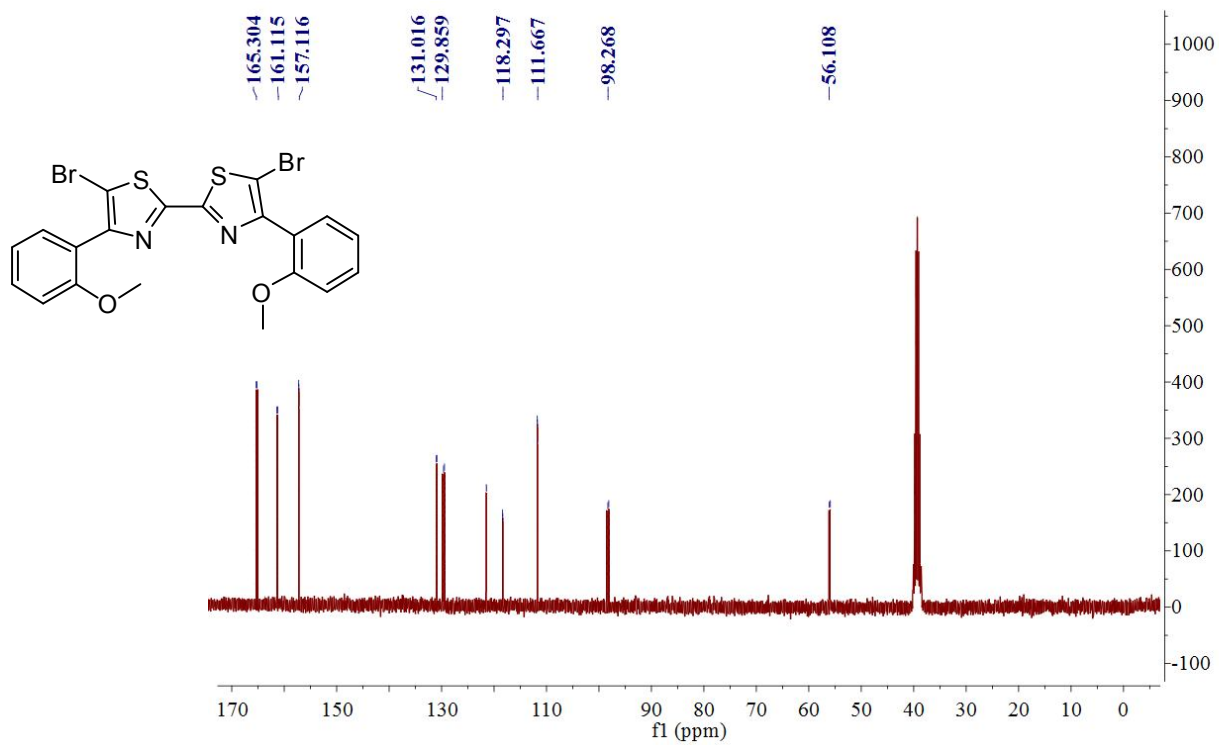


Figure S4. ¹³C NMR spectrum of the compound IV

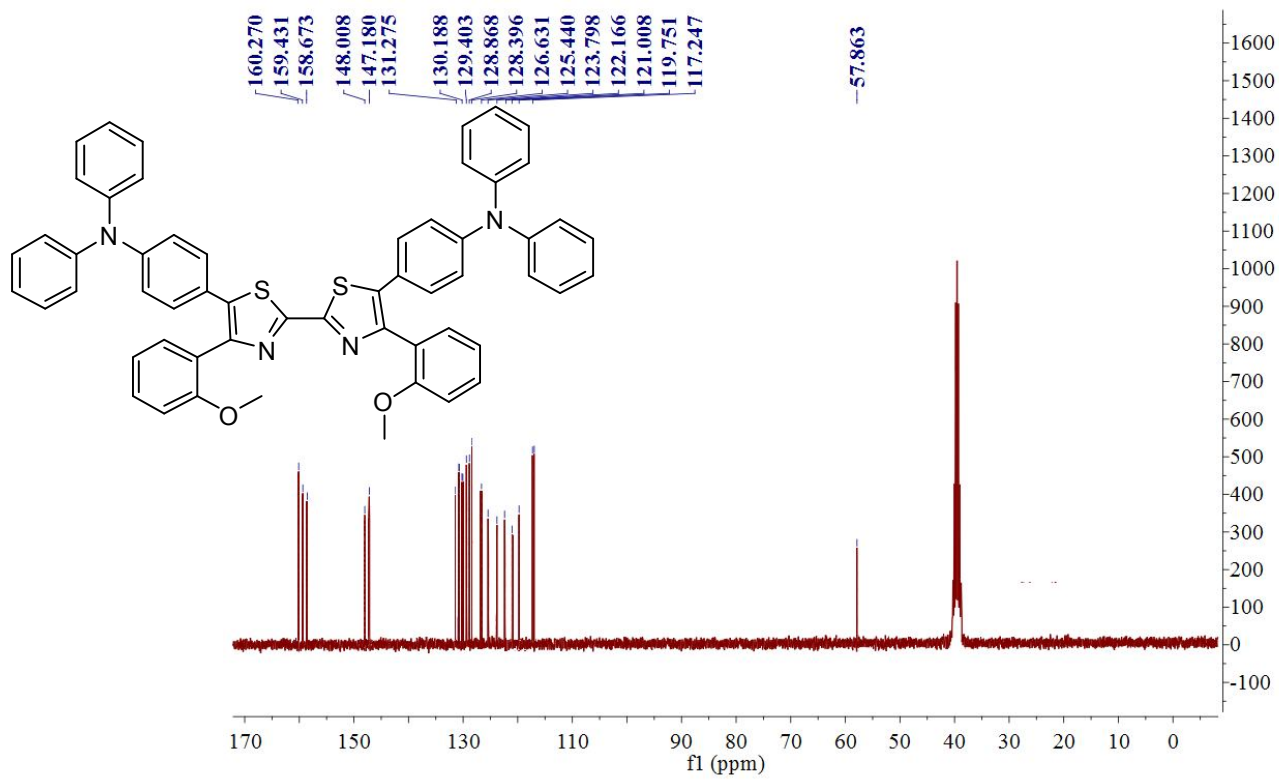


Figure S5. ¹³C NMR spectrum of the compound V

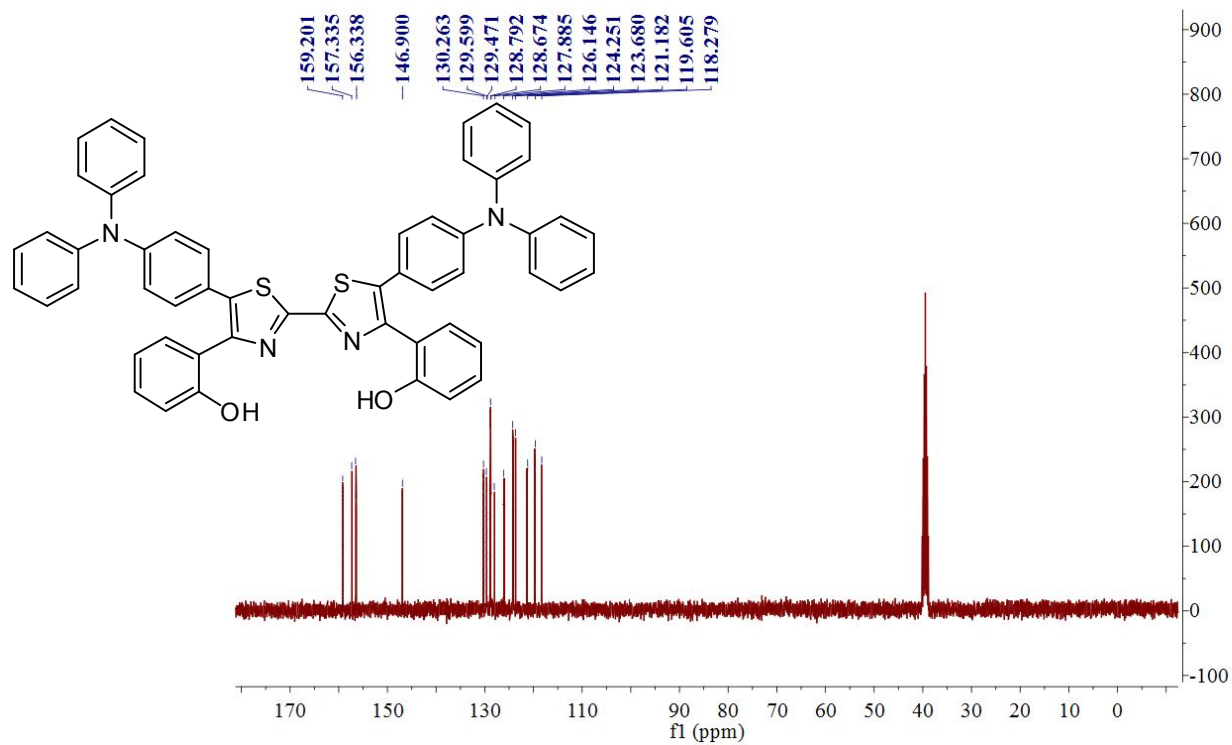


Figure S6. ^{13}C NMR spectrum of the compound 2TPABTz

H2-2#25-28 RT: 0.35-0.39 AV: 4 NL: 5.91E7
T: + c ESI Full ms [100.00-1000.00]

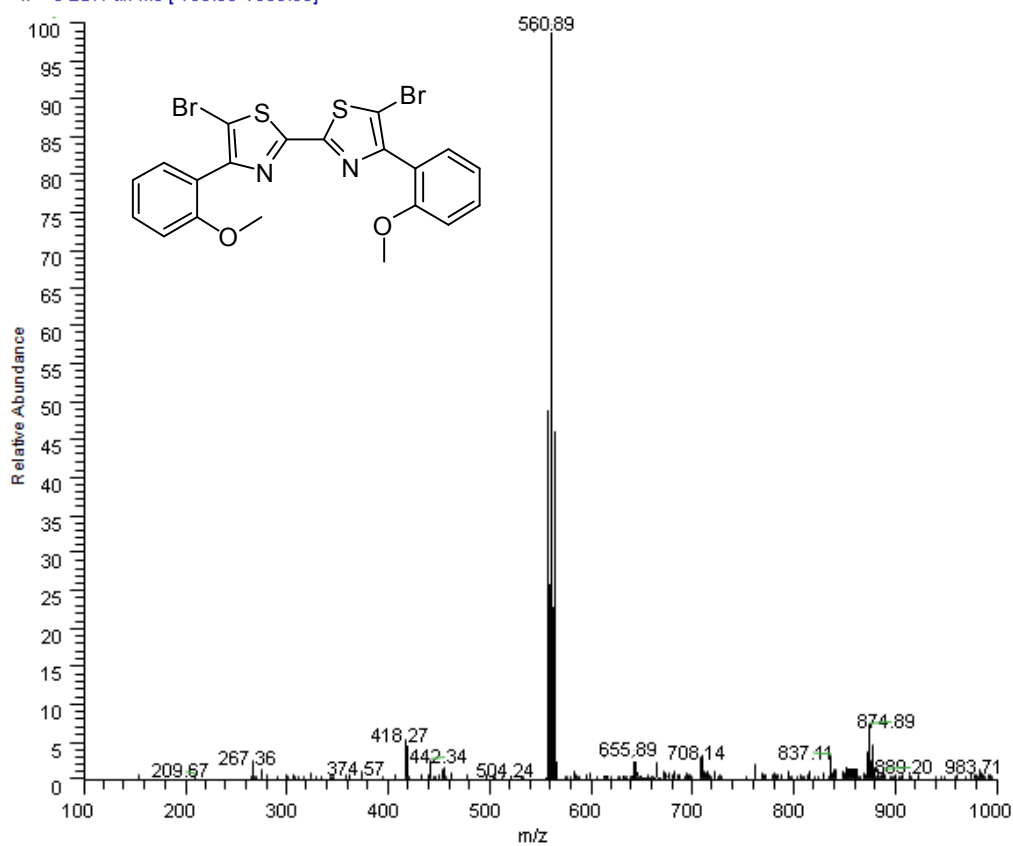


Figure S7. Mass spectrum of the compound IV

C2-2 #13 RT: 0.14 A/A: 1 NL: 3.78E7
T: + e ESI Full ms [450.00-1200.00]

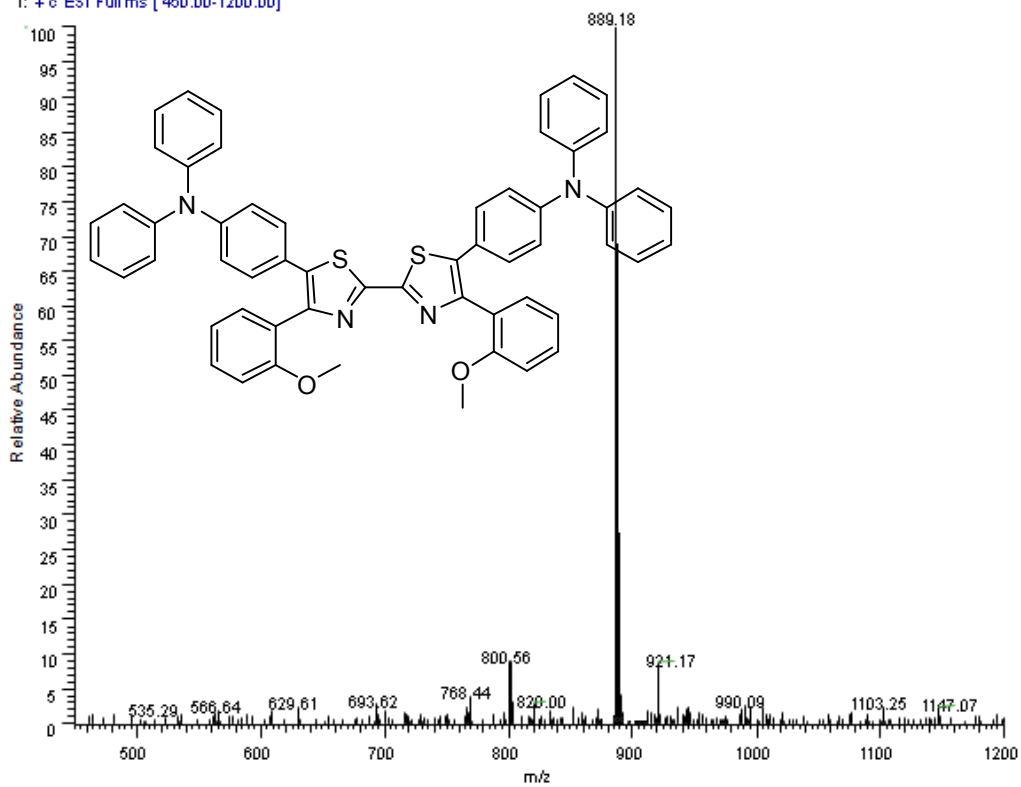


Figure S8. Mass spectrum of the compound V

p11 #5 RT: 0.05 A: 1 NL: 6.42E6
T: + c ESI Full ms [450.00-1200.00]

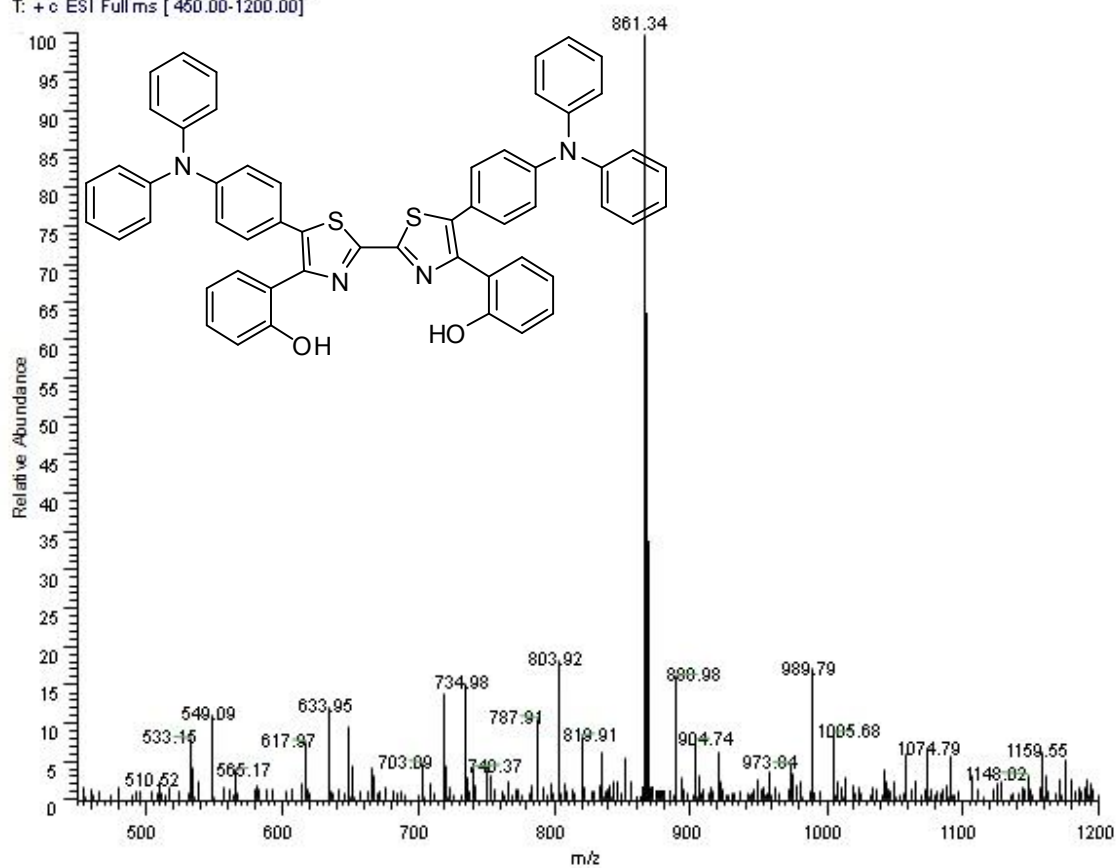


Figure S9. Mass spectrum of the compound 2TPABTz

T4-2- #7-8 RT: 0.07-0.08 A/A: 2 NL: 2.93E8
T: +c ESI Full ms [600.00-1200.00]

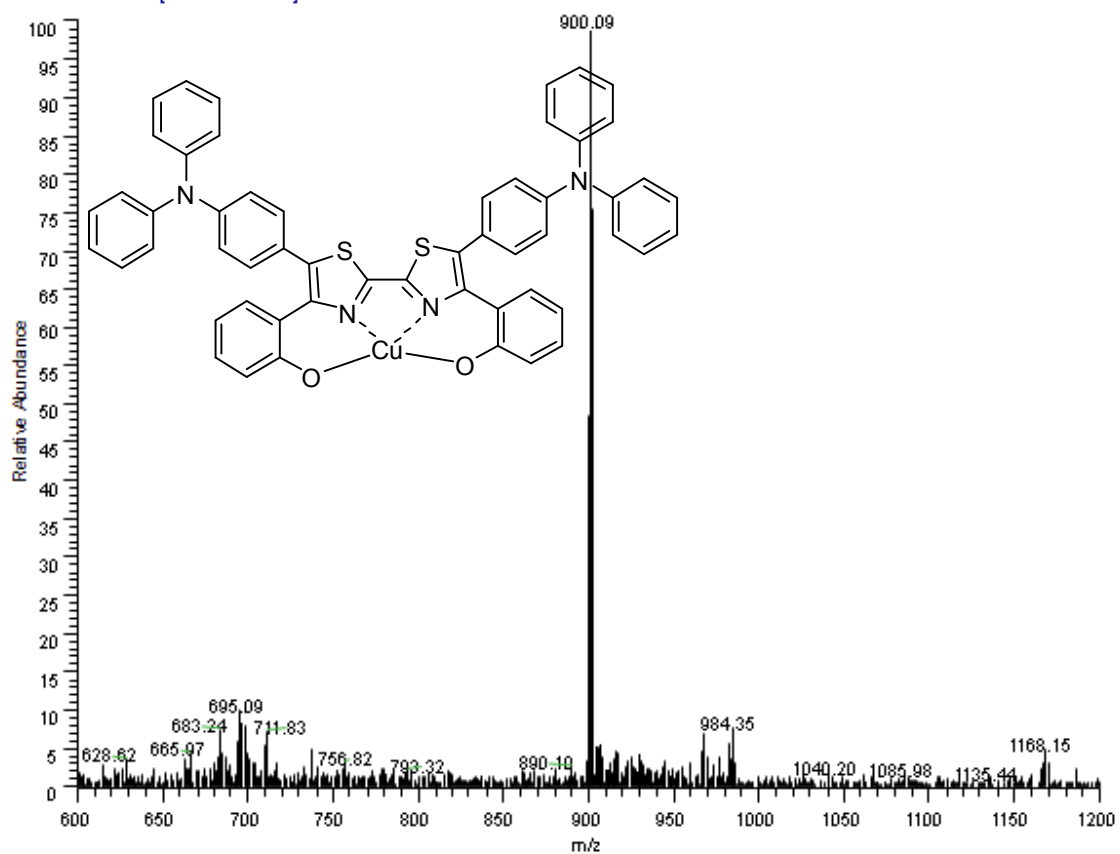


Figure S10. Mass spectrum of the complex 1

6c123bbmzb_130913103149#8 RT: 0.12 Av:1 NL: 6.20E8
T: + c ESI Full ms [500.00-1500.00]

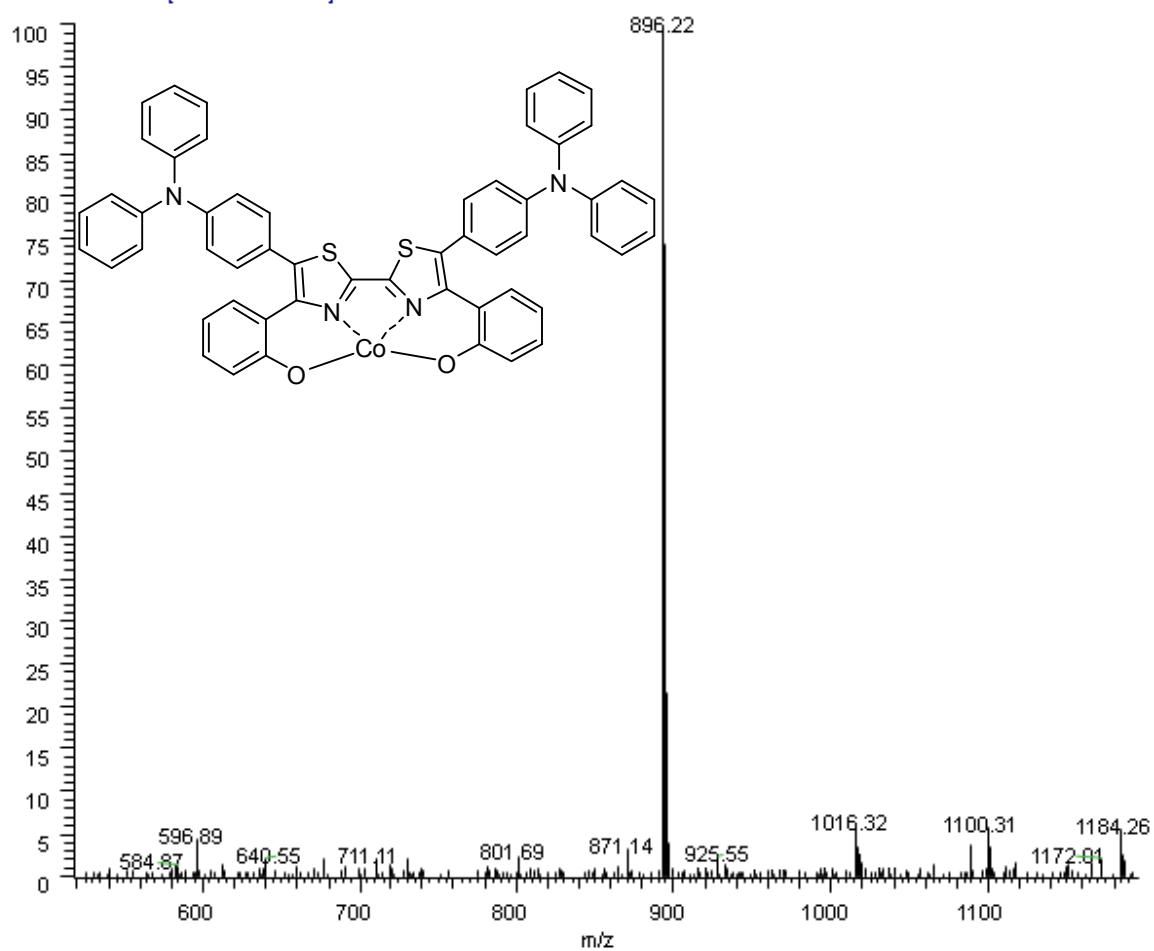


Figure S11. Mass spectrum of the complex 2

1C932BMZB#35 RT: 0.78 AV:1 NL: 2.04E8
T: + c ESI Full ms [800.00-1200.00]

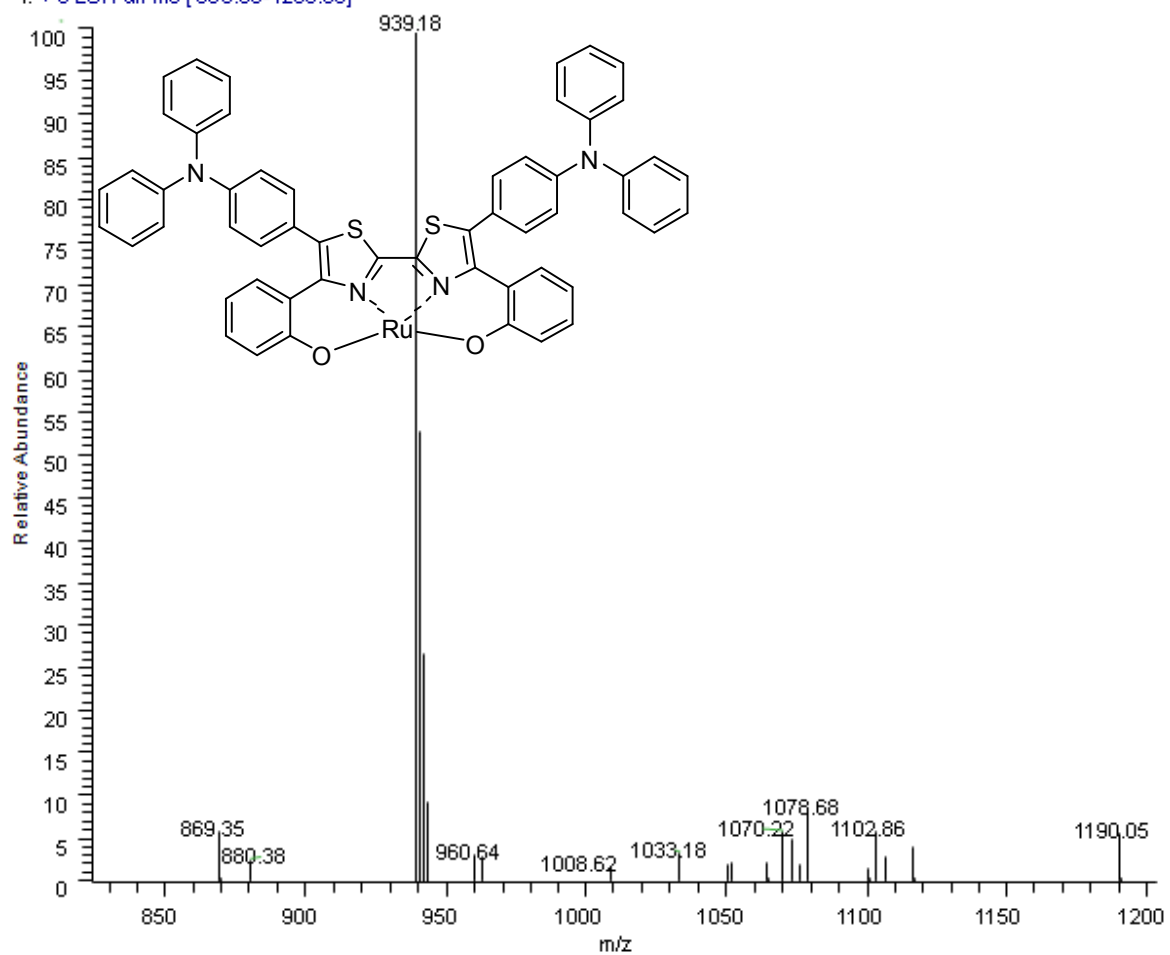


Figure S12. Mass spectrum of the complex **3**

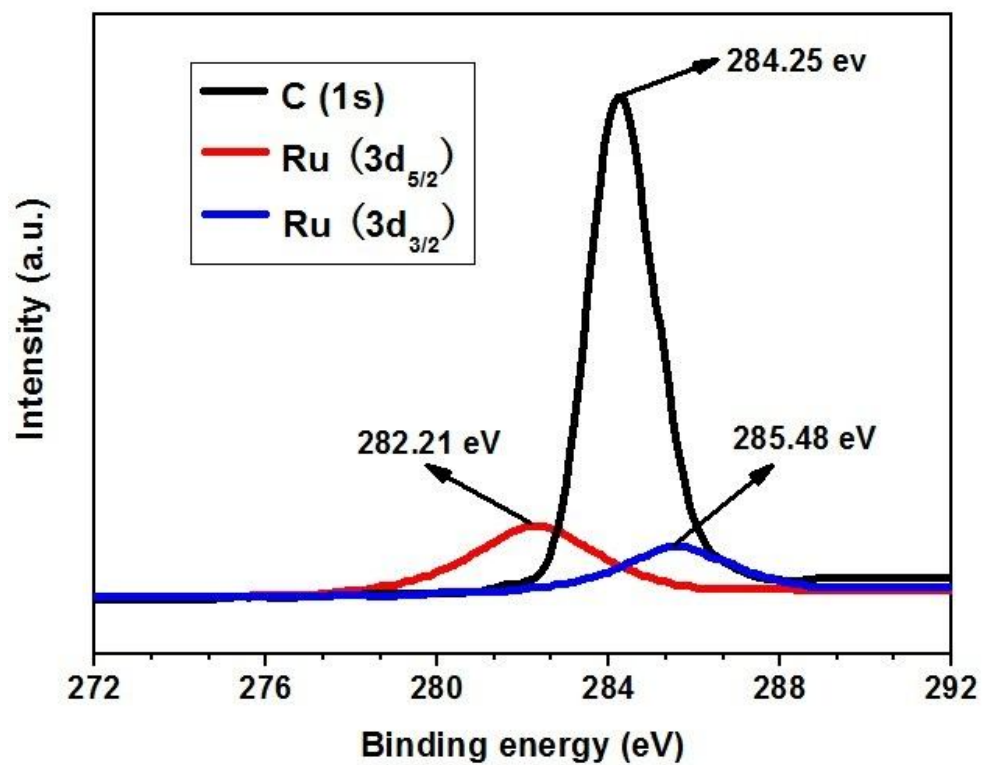


Figure S13. High-resolution XPS spectrum of the composite 6.

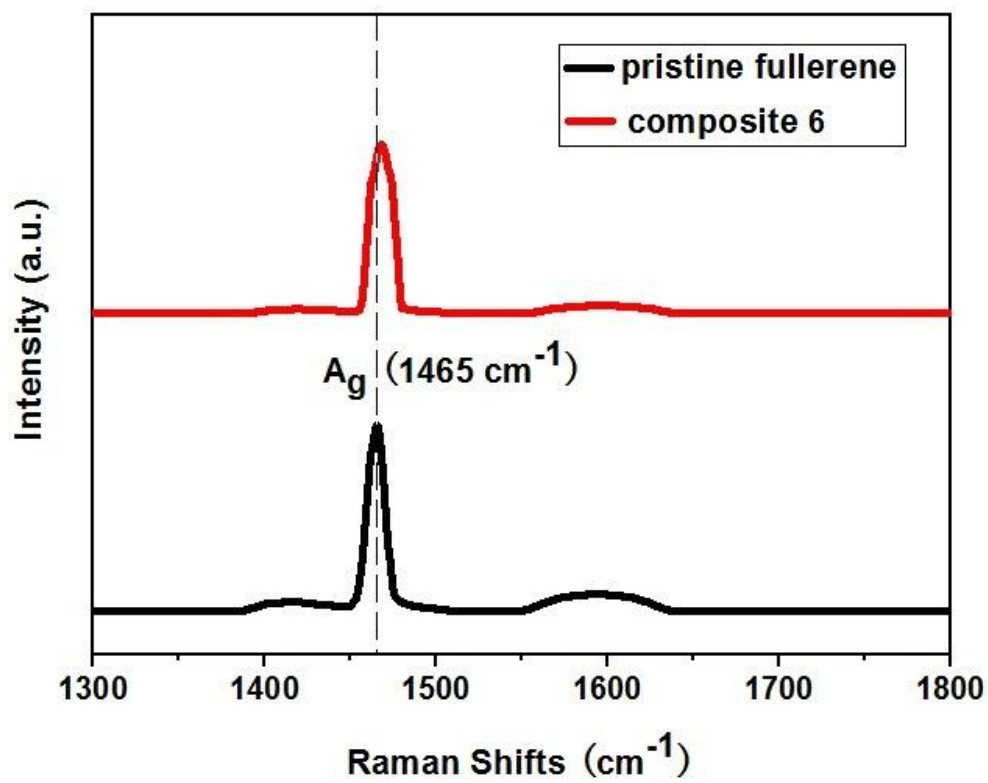


Figure S14. Raman spectra of the composite **6** and pristine C₆₀ fullerene

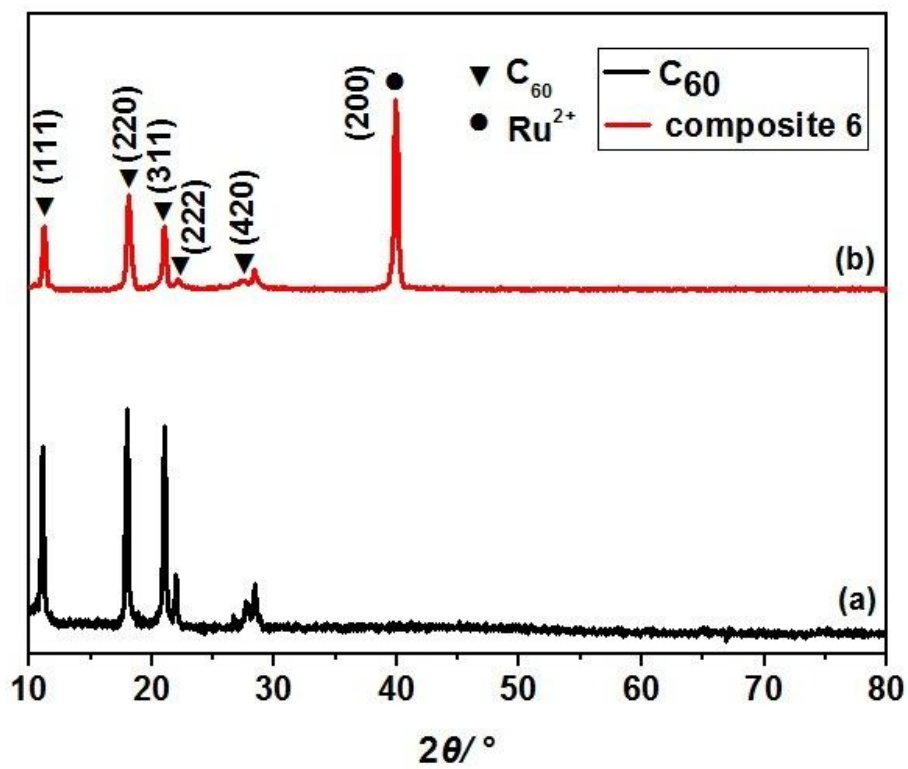


Figure S15. XRD of the composite 6 and pristine C_{60} fullerene

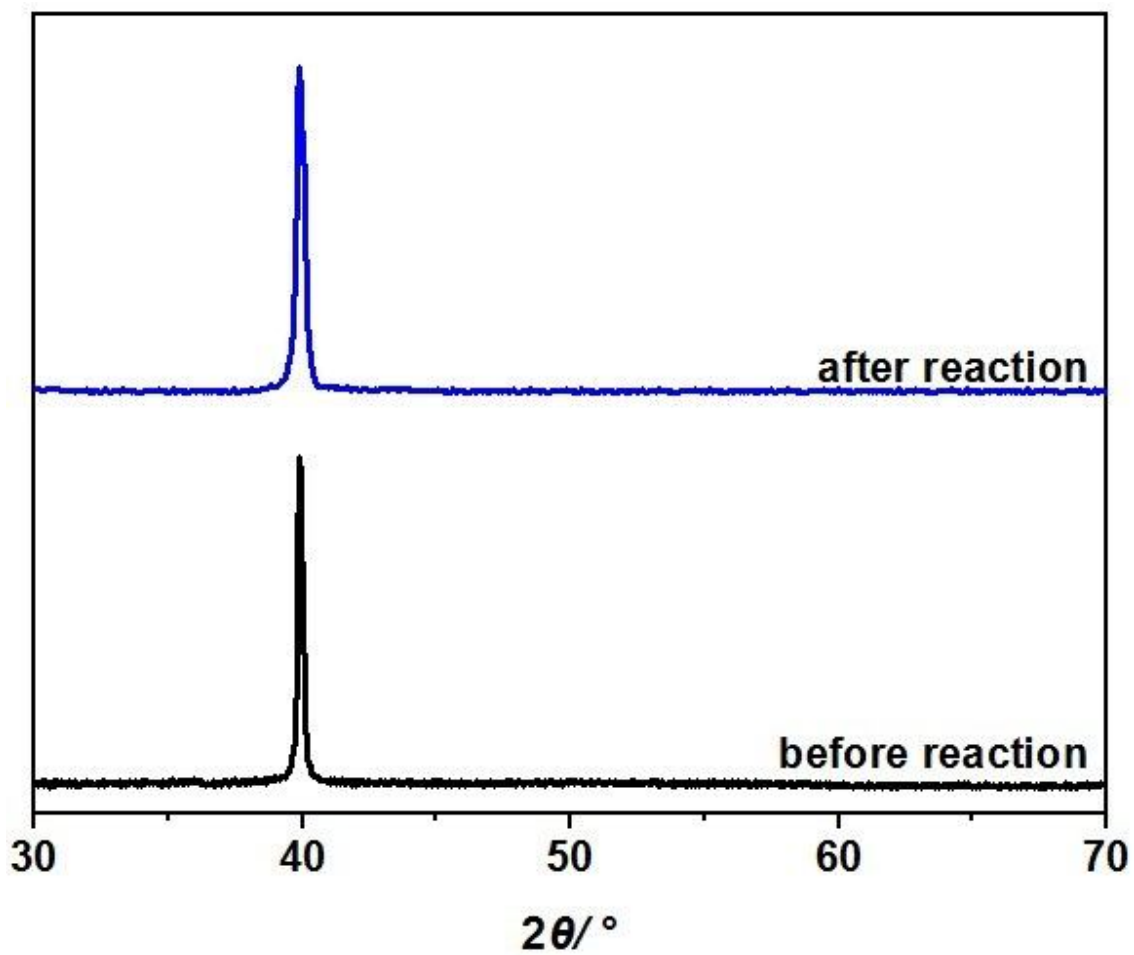


Figure S16. XRD patterns of composite **6** (2.0 wt% C₆₀) before and after the stability test.