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Electronical Supporting Information

Deprotection strategy of BODIPY conjugated microporous polymer to obtain Heterogeneous Dipyrrin/Bipyridin Ruthenium (II) complex as visible light photocatalyst

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EXPERIMENTAL SECTION

Materials. Solvents were dried by standard methods or by elution through a PureSolv Innovative Technology column drying system. Unless otherwise noted, reagents were commercially available and used without further purification.

Characterization Methods.

Synthesis. The synthesis of homogeneous and heterogeneous Ru complex was carried out using a Microwave model Discover-S from CEM Corporation.

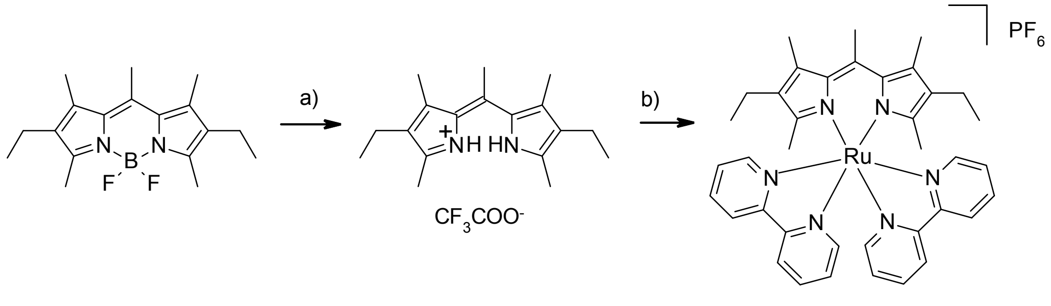
Chemical Composition. Microanalyses were made with a Carlo Erba EA1108 elemental analyzer (C, H, N). Energy-dispersive X-ray spectroscopy (EDX) measurements of the CMPBDPs were made in a Philips Model XL30 ESEM. Thermogravimetric and differential thermal analyses (TGA) were conducted in an air stream with a TA Instruments Model TA-Q500 analyzer. The samples were heated under a helium stream from 40 °C to 800°C with a heating rate of 10 °C min^{-1} in a high resolution mode. Fourier transform infrared (FTIR) spectra were recorded on a Perkin−Elmer Spectrum One spectrometer and are reported in terms of the frequency of absorption (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Model AV300 spectrometer (Larmor frequencies of 75 and 300 MHz for 13C and 1H, respectively) for liquids and a Bruker AV400WB spectrometer (Larmor frequencies of 400, 100 and 161 MHz for 13C and 1H, respectively) using 4-mm MAS probes spinning at a rate of 10 kHz for 13C solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements. The 13C CP-MAS spectra were obtained using a contact time of 3.5 ms and a relaxation time of 4 s. The number of scans used for the 13C CP-MAS spectra was 1024. High resolution mass spectra (HRMS) were recorded in an Agilent 1200 Series LC system (equipped with a binary pump, an autosampler, and a column oven) coupled to a 6520 quadrupole-time of flight (QTOF) mass spectrometer. Acetonitrile/water (75:25, v:v) was used as mobile phase at 0.2 mL min^{-1}. The ionization source was an ESI interface working in the positive-ion mode.

Textural Characterization. Nitrogen adsorption and desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2020 instrument. Prior to measurement, the samples were degassed for 12 h at 200 °C. The surface area was determined by BET (Brunauer-Emmett-Teller) theory and pore size average was determined using the Barrett−Joyner−Halenda (BJH) method. Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi Model SU-8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface. Fluorescence microscopy pictures were taken with Nikon Eclipse T2000-s microscope using TexaRed filter from Nikon.

Reaction following. GC-MS analyses were carried out using a Hewlett-Packard 7890 gas chromatograph coupled to a 5975 quadrupole mass detector (both from Agilent, PaloAlto,CA), using helium as carrier gas at ~ 1 mL min^{-1}. A 30 m × 0.25 mm i.d. × 0.25 µm film thickness fused silica column coated with SPB-1 (cross-linked methyl silicone) from Supelco (Bellefonte, PA) was used. Oven temperature was programmed from 170 °C to 300 °C at a heating rate of 10 °C min^{-1}. The injector was kept at 250 °C, and injections were made in split mode with a split ratio 1:20. Mass spectrometer was operated in electronic impact (EI) mode at 70 eV, scanning the m/z 35-600 range. Interface and source temperatures were 280 and 230 °C, respectively. Acquisition was done using HPChem Station software (Hewlett-Packard, Palo Alto, CA).

Synthesis of CMPBDPP In a 50 mL Schlenk tube were added diiodine BODIPY, 1,3,5,7,8-pentamethyl-2,6-diiodo-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene **1**, (0.495 mmol, 255 mg), 4,4''-diethynyl-5'-(4-ethynylphenyl)-1,1':3',1''-terphenyl[1] **2** (0.330 mmol, 125 mg), $[Pd\text{-}(PPh)_3]_4$ (0.013 mmol, 15 mg), CuI (0.03 mmol, 5 mg), freshly distilled DMF (10 mL) and triethylamine (5 mL). The resulting suspension was deaerated by bubbling argon at 80 °C for 20 min. The reaction mixture was stirred at 80 °C for three days under static argon. The solid obtained was washed with large amount of clean DMF, water and THF. To remove the Pd(0) the solid was stirred in a THF/water (1:1 v/v) solution with an excess of KCN. It was obtained 312 mg of a red solid. Elemental analysis (C, H, N) results are show in Table S1.

Synthesis of CMPBDPP-Ru. The heterogeneous catalyst was synthesized in two steps. 1) To a suspension of CMPBDP (70 mg) in dichloromethane were added 20 µL of BBr_3 (1 M in hexane) and it was vigorously stirred for 1 h. The solvent was removed at reduced pressure and, then, re-dispersed in a mixture water/acetone (1:9 v/v) and stirred during an hour more. Afterwards, the solid was filtered and washed with acetone. 2) In a MW tube were added the former solid with $Ru(bpy)_2Cl_2$ (4.8 mg, 0.01 mmol), trimethylamine (3 µL, 0.02 mmol) and 3 mL of ethylenglycol. The microwave conditions were 100 °C, 35 min. Afterwards, an aqueous solution of NH_4PF_6 (33 mg mL^{-1}) was added and the dispersion was stirred overnight. Then, the solid was filtered and washed with water, ethanol, dichloromethane and diethyl ether (the solution was colourless, indicative of the reaction), obtaining 75 mg. Elemental analysis (C, H, N, Ru) results are show in Table S1.

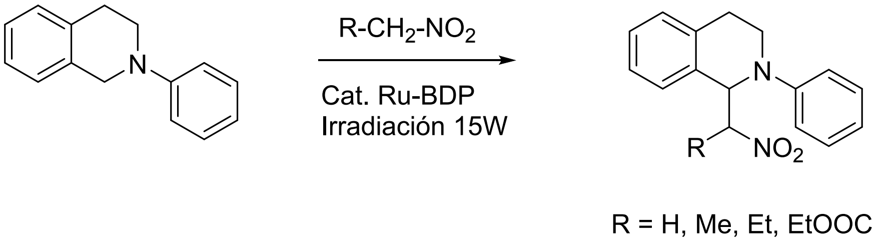


PM567 PM567-dypirrin [Ru(bdy)$_2$(dpm)]PF$_6$

Synthesis of [Ru(bpy)$_2$(dpm)]PF$_6$. The homogeneous catalyst was synthesized in two steps: a) *Deprotection of BODIPY with TFA and synthesis of PM567-dipyrrin*. The commercial BODIPY dye PM567 (318 mg, 1 mmol) was dissolved in a TFA/dichloromethane/water (90:5:5, 10 mM) mixture. The reaction mixture was stirred at room temperature for 6 h and concentrated to reduced pressure. The residue was extracted with dichloromethane, washed with water and dried with sodium sulphate. An orange solid (268 mg, 99%) was obtained. ^{1}H-NMR (300 MHz): δ= 10.45 (bs, 1H, NH), 7.75 (bs, 1H, NH), 2.68 (s, 3H, CH$_3$), 2.44 (c, 4H, J = 7.6 Hz, C*H*$_2$CH$_3$), 2.40 (s, 6H, CH$_3$), 2.15 (s, 6H, CH$_3$), 1.07 (t, 3H, J = 7.6 Hz, C*H*$_3$CH$_2$) ppm. b) *Synthesis of [Ru(bpy)$_2$(dpm)]PF$_6$.* Following the procedure described by Smalley *et al.*,[2] in a microwave reactor were dissolved PM567-dipyrrin (40 mg, 0.104 mmol), Ru(bpy)$_2$Cl$_2$[3] (45.6 mg, 0.094 mmol) and trimethylamine (60 μL, 0.4 mmol) in 1 mL of ethylenglycol. The solution was reacted in a microwave synthesizer at controlled temperature conditions 100 °C for 35 min. NH$_4$PF$_6$ (141 mg, 0.9 mmol) was dissolved in ionized water and added to the reaction mixture. The suspension was stirred overnight at room temperature and the dark precipitated collected by filtration. The precipitated was re-dissolved in acetonitrile and re-precipitated with diethyl ether. The resulting precipitated was collected by filtration, washed with diethyl ether and dried under vacuum yielding 60 mg (80%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.74 (d, J = 8.1 Hz, 4H), 8.05 (m, 4H), 7.89 (d, J = 6.3 Hz, 4H), 7.77 (d, J = 5.5 Hz, 2H), 2.68 (s, 3H, CH$_3$), 2.44 (c, 4H, J = 7.6 Hz, C*H*$_2$CH$_3$), 2.40 (s, 6H, CH$_3$), 2.2 (s, 6H, CH$_3$), 1.25 (t, 3H, J = 7.6 Hz, C*H*$_3$CH$_2$); ESI-MS (+): m/z 683.3 ($C_{38}H_{41}N_6Ru^{+1}$, M$^+$+1); ESI-MS (-): m/z 144.9 (M$^-$, PF$_6^-$).

2’)

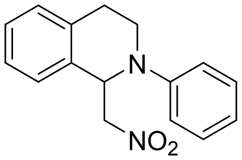
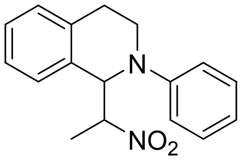
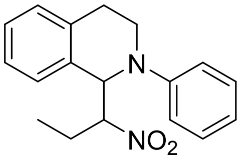
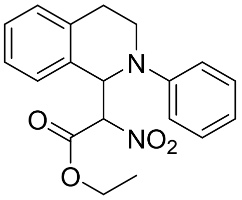
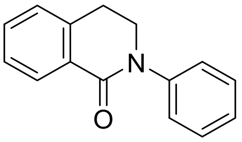
Synthesis of tetrahydroisoquinoline. The synthesis was carried out following the procedure described by. Li et al.[4] from tetrahydroisoquinoline with a 40 % yield.



General procedure of iminium ion generation and trapping photocatalyzed by CMPBDP-Ru. A mixture of tetrahydroisoquinoline (6.25 mg, 0.03 mmol), Ru catalyst (5 mg for CMPBDP-Ru, 0.0003 mmol, Ru 1 mol%) and the nitro compound (1 mL) was stirred at room temperature while is irradiated under a 15 W LED light. The reaction was followed by GC-MS. When 2-phenylisoindoline has disappeared, DCM and Et_2O were added and centrifuged in order to separate liquid and solid phases. The recovered catalyst was washed with Et_2O several times, dried and reused when needed. The liquid extract was evaporated under reduced pressure and analyse by ^{1}H-NMR.

The structures detected by GC-MS were confirmed by HRMS, the results are in Table S1:

Table S1: Results of ^{1}H-RMS analysis.

Molecular structure	Molecular formula	Theoretical mass	Experimental mass	|Δm| (ppm)	Detected species
	$C_{16}H_{16}N_2O_2$	268.12118	268.1214	0.82	$[M+H]^+$
	$C_{17}H_{18}N_2O_2$	282.13683	282.13727	1.55	$[M+H]^+$
	$C_{18}H_{20}N_2O_2$	296.15248	296.1528	1.09	$[M+H]^+$
	$C_{19}H_{20}N_2O_4$	340.14231	340.14178	1.56	$[M+H]^+$
	$C_{15}H_{13}NO$	223.09971	223.09985	0.60	$[M+H]^+$

Additional Figures:

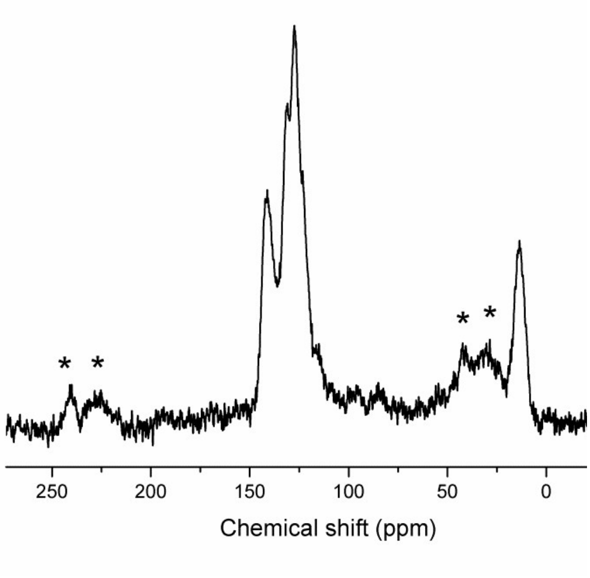


Figure S1. ^{13}C-NMR (CP/CP MAS) spectra of **CMPBDP-2.** Side bands have been marked (*).

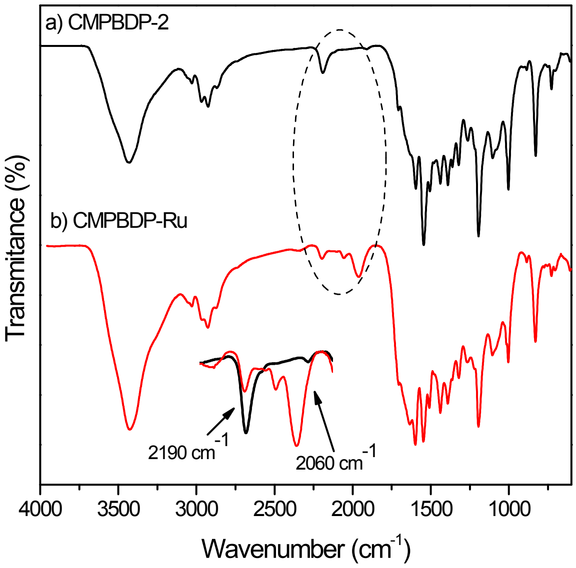


Figure S2. FTIR spectra of the polymer networks **CMPBDP-2** (a), **CMPBDP-Ru** (b). Inset: details between 1800-2400 cm^{-1}.

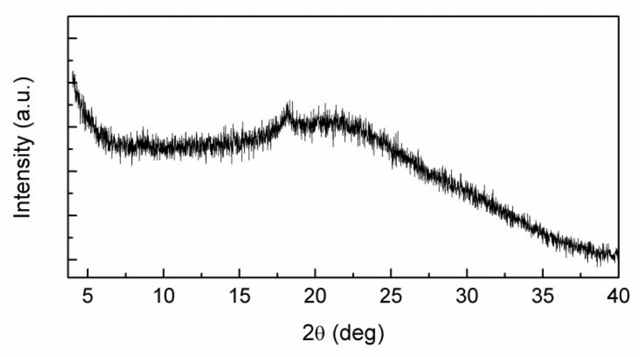


Figure S3. PXRD pattern of CMPBDP-2.

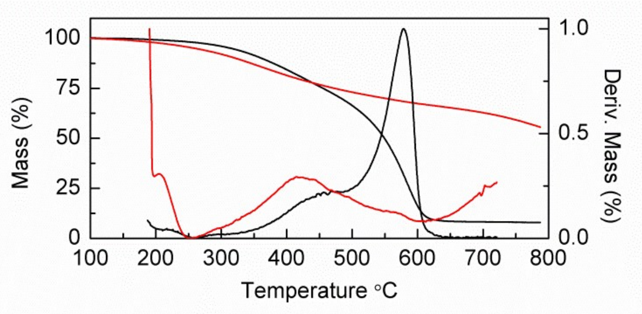


Figure S4. Thermogravimetric analysis of CMPBDP-2 (black) and CMPBDP-Ru (red).

Table S2. Elemental analysis.[a]

	Chemical Formula	Calc. (%)				Found (%)			
		C	H	N	Ru	C	H	N	Ru[b]
CMPBDP-2	$C_{30}H_{15}(C_{14}H_{15}BF_2N_2)_{1.5}$	80.01	4.94	5.49	--	71.51	5.5	6.94	--
CMPBDP-Ru	$C_{30}H_{15}(C_{14}H_{15}BF_2N_2)_{1.44}(C_{34}H_{31}N_4Ru)_{0.06}$	79.79	4.93	5.56	0.77	69.95	5.29	5.45	0.61

[a] Elemental analysis shows that the experimental values of C and H are lower and of N is slightly higher than the corresponding theoretical values calculated for an ideal structure. It is very well known that this kind of materials show bad combustion together with the fact the fluorine atoms present in BODIPY dyes lead to bad combustion and incorrect values in the elemental analysis in molecular compounds. Note that the Pd content results of the Sonogashira reaction has been removed with the post-treatment of CMPBDP-2 solid with an aqueous solution of potassium cyanide (KCN). In fact, the Pd content was less of 0.04% measured by inductively coupled plasma spectroscopy.

[b] measured by ICP.

References

(1) Weber. *J. Chem. Soc. Perkin Trans. II* **1988**, 1251.

(2) Smalley, S. J.; Waterland, M. R.; Telfer, S. G. *Inorg. Chem.* **2009**, *48* (1), 13–15.

(3) Sulliva, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17* (12), 3334–3341.

(4) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127* (19), 6968–6969.