C-H activation derived CPPs for photocatalytic hydrogen production excellently accelerated by DMF cosolvent

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Instruments and Methods.

Solid state magic angle spinning ¹³C CP/MAS NMR measurement was carried out on a Bruker Avance 400 model 400 MHz NMR spectrometer at a MAS rate of 10 kHz. FT-IR spectrum was measured on a FT-IR spectrometer (Bruker, ALPHA) in transmission mode at room temperature. Thermal properties of the polymer networks were evaluated using thermogravimetric analysis (TGA) with a differential thermal analysis instrument (STA2500, NETZSCH) over the temperature range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. High resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 90° on Thermo ESCALAB 250XI (Thermo Fisher Scientific, USA) with an Ala X-ray line (1486.6 eV). Theoretical calculations based on density functional methods have been performed for **CPs1~4** with Gaussian09 program. Becke's three-parameter gradient-corrected functional (B3LYP) with 6-31G(d,p) basis was used to optimize the geometry.

Morphology of the polymer networks was obtained using a field emission scanning electron microscope (SEM, MLA650F, American) and transmission electron microscope (TEM, Tecnai G2-20, American). Surface areas and pore size distributions were measured by N₂ adsorption and desorption at 77.3 K using an ASAP 2020 HD88 (Micromeritics) volumetric adsorption analyzer. Surface area was calculated in the relative pressure (P/P0) ranging from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the N₂ adsorption branch using non-local density functional theory (NL–DFT). Sample was degassed at 120 °C for 12 h under vacuum (10–5 bar) before analysis.

UV-vis diffuse reflection spectrum was obtained for the dry pressed disk samples using a scanning UV-vis spectrophotometer (UV-2600, SHIMADZU, Japan) equipped with an integrating sphere assembly, using BaSO₄ as a reflectance sample. Fluorescent spectrum of the polymers was measured with a HITACHI F-4600 PC fluorescence spectrometer by using excitation wavelength of 467 nm at room temperature. Time-resolved fluorescence spectroscopy was performed on HORIBA Instruments FL-1000 fluorescence spectrometer. The photocurrents were recorded by an electrochemical workstation (CHI650E/700E., Shanghai) equipped with a conventional three-electrode cell. A platinum plate electrode and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrodes were immersed in a sodium sulfate electrolyte solution (0.1 M). The working electrode was illuminated by a 300 W Xe lamp (Beijing Perfect Light, PLS-SXE300) from the backside to minimize the impact of thickness of the semiconductor layer.

Cyclic voltammetry (CV) measurement was carried out on a CHI660E (Chenhua, Shanghai) electrochemical workstation in a three electrode-cell system: glassy carbon electrode as the working electrode, saturated calomel electrode (SCE) electrode as the reference electrode, platinum wire as the counter electrode. The polymer was mixed with 5 wt% chitosan, the mixture was dropped cast on a glassy carbon working electrode and let the solvent evaporate at room temperature for 4 h. The measurement was carried out in a solution of tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in acetonitrile with a scan rate of 100 mV s⁻¹ in the range of -2 V to 1.5 V.

Pd contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, IRIS Intrepid II), where the sample was digested in HNO₃/HCl (1/1, v/v) at 265 °C, then raised the temprature to 300 °C, added HClO₄, then added HNO₃ to extract after steaming, and diluted it by ultrapure water and filtered.



Fig. S1 Catalytic cycle of Pd-catalyzed C-H/C-X coupling that involves $Pd^0 \leftrightarrow Pd^{II}$ interchange (a), XPS spectra of **CP1** (b) survey and (c) Pd3d.



Fig. S2 FT-IR spectra of as-prepared CPs1~4.







Fig. S4 DFT-optimized structures of repeat units of CPs1~4.

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Fig. S6 CV curves of CPs1~4.



Fig. S7 HERs of **CP1** dispersed in AA/DMF, AA/MeOH, TEOA/MeOH, Glc/DMF and Glc/MeOH water solutions under visible light irradiation.



Scheme S1. (a) Resonance structures of DMF. (b) Hydrogen bond interaction between DMF and H₂O.

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Catalysts	Co-	SA	Illumination	HER (µmol g-	Refs.
	catal.			¹ h ⁻¹)	
PyDOBT-1	Pt	TEOA	Full wavelength	12,968	Macromolecules 2018, 51,
PyDOBT-1	-	TEOA	Visible light	5697	9502.
DBTD-CMP1	Pt	TEOA	Full wavelength	9200	ACS Catal. 2018, 8, 8590.
B-BT-1,4	Pt	TEOA	Visible light	2320	Angew. Chem. Int. Ed. 2016,
					55, 9202.
PyBT-2	Pt	TEOA	Full wavelength	1062	Appl. Catal. B: Environ.
					2018 , <i>228</i> , 1.
P-FSO	-	TEOA	Visible light	8000	Appl. Catal. B: Environ.
					2019 , <i>245</i> , 596.
P7	-	TEA	Full wavelength	5800	Angew. Chem. 2016,
					128,1824.
PCP4e	-	TEA	Visible light	9429	J. Am. Chem. Soc. 2016, 138:
					7681.
LDC-S-TiO ₂	Pt	MeOH	Full wavelength	12,505	Adv. Sci. 2018, 5, 1700870
PTh-c	Pt	AA	Visible light	2800	Appl. Catal. B: Environ.
					2017 , <i>211</i> , 98.
FS-COF	Pt	AA	Visible light	16,300	Nat. Chem. 2018, 10, 1180.
CP1	-	AA	Visible light	15,980	this study
CP1	Pt	AA	Visible light	30,810	this study





Fig. S8 PHP performances of CPs1~4 (6 mg) dispersed in AA/DMF/H₂O under visible light irradiation.



Fig. S9 Uv-vis spectrum of **CP1** ultrasonically dispersed in DMF/H₂O mixed solution, and the corresponding AQY values of **CP1**/AA/DMF/H₂O suspension irradiated by different monochromatic light.



Fig. S10 FT-IR spectra of CP1 before and after cycle test.



Fig. S11 Uv-vis spectra of CP1 before and after cycle test.



Fig. S12 PHP performances of **CP1** (6 mg) with and without Pt-cocatalyst in AA/DMF/H₂O solutions under visible light irradiation.