Supporting Information for

Carbazole and thiophene containing conjugated microporous polymers with varying

planarity for enhanced photocatalytic hydrogen evolution

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S1. Materials

Raw chemical materials and solvents were purchased from commercial resources and then used as it is. Carbazole (95%), 2,5-thiophenediylbisboronic acid (Th-2BO, 95%), and n-bromosuccinimide (99%) were received from Acros. Potassium permanganate as well as potassium carbonate were purchased from Sigma–Aldrich. tetrakis(triphenylphosphine) palladium(0) (99%) was obtained from J. T. Baker.

S2. Characterization

A Bruker Tensor 27 FTIR spectrophotometer was used to measure FTIR spectra via KBr disk method; every scan was recorded by 4 cm⁻¹ resolution range. An INOVA 500 instrument was employed for recording ¹³C NMR and ¹H spectra by DMSO-d₆ and CDCl₃ as solvents and tetramethylesilane (TMS) as exterior standard. Chemical shifts are recorded by part per million (ppm) scale. Bruker Avance 400 NMR spectrometer in addition to a Bruker magic-angle-spinning (MAS) sensor were applied for recording Solid state nuclear magnetic resonance (SSNMR) spectra. ¹³C NMR spectral information were registered at 75.5 MHz via cross-polarization with MAS (CPMAS), the CP contact time was 2 ms, during data acquiring ¹H decoupling was applied by a decoupling frequency 32 KHz and MAS sample spinning rate 10 kHz. Micromeritics ASAP 2020 surface area in addition to porosity analyzer were employed for the BET surface areas and porosimetry records of the synthesized matrixes (ca. 20–100 mg) during gradual exposure to high purity N_2 (up to ca. 1 atm) in a liquid N₂ (77 K) bath nitrogen isotherms were created. TA Q-50 analyzer under a flow of N₂, TGA data were examined. In a well-sealed Pt cell and under nitrogen flow rate 50 mL min⁻¹; samples were exposed to raising heat from 40 to 800 °C, at heating ramp 20 °C min⁻¹. A JEOL JSM-7610F scanning electron microscope was used for visualization of FE-SEM, samples were exposed to Pt sputtering for 100 s for handling observation. A JEOL-2100 scanning electron microscope, operated at 200 kV was used for TEM images. Suitable organic solvents were applied for dispersing samples in a quartz cell ($0.2 \times 1.0 \times 4.5 \text{ cm}^3$) for fluorescence spectroscopy which measured by LbGude X350 spectrometer. Photoluminescence (PL) analyses were recorded via Hitachi 11 F-7000 spectrophotometer equipped with a Xenon lamp ($\lambda = 250 \sim 800 \text{ nm}$) and a Hitachi U-3300 spectrophotometer was employed for measuring UV-visible absorption spectra of synthesized CMPs.

S3. Synthetic Procedures



Scheme S1. Synthesis of 9-(4-bromophenyl)-9H-carbazole (Cz-Br) and 3,6-dibromo-9-(4-bromophenyl)-9H-carbazole (Cz-3Br)

Synthesis of 9-(4-bromophenyl)-9H-carbazole (Cz-Br): A mixture of carbazole (2 g, 12 mmol), 1-bromo-4-iodobenzene (5.07 g, 17.8 mmol), potassium carbonate (6.62 g, 48 mmol), and Cu powder (1.53 g, 27 mmol) was evacuated up to 30 min followed by addition of DMF (20 mL) then freeze-pumb-thaw process for three times. The reaction was left under nitrogen atmosphere for next 3 days at 130 ° C. The solid was separated then washed by plenty of water, after that it was washed again by methanol following by drying to afford Cz-Br (83%). ¹H NMR (CDCl₃, 25 °C, 500 MHz): δ = 8.22 (d, *J* = 8 Hz, 2H), 7.83 (d, *J* =

8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8 Hz, 2H), 7.29 (t, *J* = 8 Hz, 2H).¹³C NMR (CDCl₃, 25 °C, 125 MHz): 140.66 , 136.96, 133.91, 129.55, 127.10, 125.53, 121.25, 121.00, 120.89, 110.19. Anal. Calcd. for C₁₈H₁₂BrN (322.21): C, 67.10; H, 3.75; Br, 24.80; N, 4.35 Found: C, 68.06; H, 3.91; Br, 24.01; N, 4.02.

Synthesis of 3,6-dibromo-9-(4-bromophenyl)-9H-carbazole (Cz-3Br): In an ice-bath for 30 min; Cz-Br (1.0 g, 3.10 mmol) was added to DCM (17 mL) and NBS (1.36 g, 7.69 mmol) under magnetic stirring. Furthermore, the mixture was left overnight under N₂ environment with continuous stirring. The reaction was quenched with water and the product was extracted with dichloromethane (3 × 40 mL). The combined organic extracts were dried over anhydrous MgSO₄, and filtered. The organic layer was then evaporated under reduced pressure followed by purification using a silica gel chromatography with hexane as the eluent to afford Cz-3Br (90%) as a crystalline white solid. ¹H NMR (CDCl₃, 25 °C, 500 MHz): 8.58 (s, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 9 Hz, 2H).¹³C NMR (CDCl₃, 25 °C, 125 MHz): 139.83, 136.03, 133.97, 130.22, 129.58, 124.38, 121.56, 113.26, 112.48, 112.45. m/z (EI, 70 eV) 480.83 [M⁺] (100%). Anal. Calcd. for C₁₈H₁₀Br₃N (480.00): C, 45.04; H, 2.10; Br, 49.94; N, 2.92 Found: C, 45.88; H, 1.93; Br, 49.05; N, 3.14.



Scheme S2. Synthesis of 3,6-dibromocarbazole (Cz-2Br) and 3,3',6,6'-tetrabromo -9,9' bicarbazole (Cz-4Br).

Synthesis of 3,6-Dibromocarbazole (Cz-2Br): Previous report¹ with an inconsiderable modulation was followed for preparing 3,6-Dibromocarbazole (Cz-2Br). A suspension of carbazole (5.00 g, 30.0 mmol) dissolved in DCM (300 mL) mixed with a solution of NBS (10.7 g, 60.0 mmol) in DMF (50 mL). The reaction mixture was stirred at room temperature overnight. The solution was washed with water (3×150 mL), then the organic layer was separated, and the solvent was evaporated. The solid was washed with DCM, then collected and dried under vacuum to yield Cz-2Br (82%) as white crystals. ¹H NMR (CDCl₃, 25 °C, 500 MHz): 11.58 (NH, 1H), 8.41 (s, 2H), 7.52 (d, *J* = 8.5 Hz, 2 H), 7.42 (d, *J* = 2 Hz, 2H). ¹³C NMR (CDCl₃, 25 °C, 125 MHz): 139.42, 129.42, 124.34, 123.47, 112.97, 112.32. Anal. Calcd. for C₁₂H₇Br₂N (325.00): C, 44.35; H, 2.17; Br, 49.17; N, 4.31 Found: C, 43.21; H, 2.14; Br, 49.87; N, 4.78.

Synthesis of 3,3',6,6'-Tetrabromo-9,9'-bicarbazole (Cz-4Br): Cz-4Br was synthesized as mentioned in the previous report with incommodious modification. ^{1,2} A solution of Cz-2Br (2.00 g, 30.0 mmol) dissolved in acetone (40 mL) at 50 °C was transferred to a solution of KMnO₄ (2.92 g, 90.0 mmol) in acetone (10 mL), then the mixture was heated at 50 °C for 2 h and then hydrolyzed with water (100 mL). DCM was used for extraction and solvent evaporation. Several washing steps by MeOH were introduced to produce Cz-4Br (71%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.27 (d, 4H), 7.47 (dd, *J* = 1.8, 8.5 Hz, 4H), 6.75 (d,

J = 8.5 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 139.31, 131.19, 124.81, 123.30, 115.41, 110.59. m/z (EI, 70 eV) 647.74 [M⁺] (100%). Anal. Calcd. for C₂₄H₁₂Br₄N₂ (647.99): C, 44.49; H, 1.87; Br, 49.32; N, 4.32 Found: C, 45.08; H, 1.98; Br, 48.28; N, 4.66.



Scheme S3. Synthesis of Cz-3Th CMP.

Synthesis of Cz-3Th CMP: A mixture of Cz-3Br (139.7 mg, 0.29 mmol), Th-2BOH (74.7 mg, 0.44 mmol), tetrakis(triphenylphosphine)palladium (67 mg, 0.057 mmol) and potassium carbonate (402 mg, 2.9 mmol) were added into a Pyrex tube (25 mL) and subjected to a vacuum for 15 min followed by addition of dimethylacetamide (10.34 ml) and water (1.3 ml). The tube was evacuated through three Freeze-pump-thaw cycles. The tube was heated at 140 °C for 3 days, then the contents were separated and washed well by acetone. The solid was dried under vacuum at 120 °C overnight to afford Cz-3Th CMP as a green precipitate (yield 88%).



Scheme S4. Synthesis of Cz-4Th CMP.

Synthesis of Cz-4Th CMP: A mixture of Cz-4Br (150 mg, 0.23 mmol), Th-2BOH (79.6 mg, 0.46 mmol), tetrakis(triphenylphosphine)palladium (53.5 mg, 0.046 mmol) and potassium carbonate (320 mg, 2.3 mmol) were added into a Pyrex tube (25 mL) and subjected to a vacuum for 15 min followed by addition of dimethylacetamide (10.34 ml) and water (1.3 ml). The tube was evacuated through three Freeze-pump-thaw cycles. The tube was heated at 140 °C for 3 days, then the contents were separated and washed well by acetone. The solid was dried under vacuum at 120 °C overnight to afford Cz-4Th CMP as a green precipitate (yield 79%).

Synthesis of Cz-3Th and Cz-4Th CMPs via Stille coupling (Cz-3Th CMP-St and Cz-4Th CMP-St): A mixture of 2,5-bis(trimethylstannyl)thiophene (50 mg, 0.122 mmol) and Cz-3Br (39 mg, 0.081 mmol) or Cz-4Br (39.5 mg, 0.061 mmol) were added into a Pyrex tube (25 mL) and then dissolved in a cosolvent of *N*,*N*-dimethylformamide and toluene (1: 1 v/v, 8 mL). After degassing for 30 min tetrakis(triphenylphosphine)palladium (11 mg, 0.01 mmol) was added and subjected to further degassing for 15 min. The tube was evacuated through three Freeze-pump-thaw cycles. The tube was heated at 120 °C for 60 h, then the contents were separated and washed well by acetone, methanol and chloroform. The solid was dried under vacuum at 120 °C overnight to afford Cz-3Th CMP-St as a green precipitate (yield 82%) or Cz-4Th CMP-St as a green precipitate (yield 80%).



Fig S1. ¹H NMR of 9-(4-bromophenyl)-9H-carbazole (Cz-Br).



Fig S2. ¹³C NMR of 9-(4-bromophenyl)-9H-carbazole (Cz-Br).



Fig S3. ¹H NMR of 3,6-dibromo-9-(4-bromophenyl)-9H-carbazole (Cz-3Br).



Fig S4. ¹³C NMR of 3,6-dibromo-9-(4-bromophenyl)-9H-carbazole (Cz-3Br).



Fig S6. ¹³C-NMR of 3,6-dibromocarbazole (Cz-2Br).



Fig S7. ¹H NMR of 3,3',6,6'-tetrabromo-9,9' bicarbazole (Cz-4Br).



Fig S8. ¹³C NMR of 3,3',6,6'-tetrabromo-9,9' bicarbazole (Cz-4Br).

Explanation of spectral analyses of Cz-3Br and Cz-4Br: Fourier transform infrared (FTIR) of Cz-3Br revealed an aromatic stretching signal at 3059 cm⁻¹ in addition to the characteristic C=C stretching signals at 1492 and 1466 cm⁻¹ (Fig. 1a). The ¹H NMR spectrum of Cz-3Br presented a singlet signal at 8.58 ppm and doublet signals in a range between 7.85-7.35 ppm which attributed to the aromatic protons (Fig. S3, ESI). The ¹³C NMR profile of Cz-3Br showed a discriminated signal at 3072 cm⁻¹ and C=C stretching signals at 1467 and 1425 cm⁻¹ (Fig. 1b). The characteristic signals ranged from 8.27 to 6.75 ppm in the ¹H NMR spectrum of Cz-4Br exhibited a signal at 139.31 ppm for the C–N nuclei as well as signals for the other carbon nuclei (Fig. S8, ESI).

S5. Mass Profiles of monomers



Fig. S9 Mass spectra of (a,b) Cz-3Br and (c,d) Cz-4Br.

S6. FTIR Profiles of monomers and CMPs



Fig. S10 FTIR spectra of (a) Cz-3Br, (b) Th-2BOH, and (c) Cz-3Th CMP.



Fig. S11 FTIR spectra of (a) Cz-4Br, (b) Th-2BOH, and (c) Cz-4Th CMP.

S7. Thermal gravimetric analysis profile



Fig. S12 TGA analysis of Cz-3Th and Cz-4Th CMPs.

Table S1. Decomposition temperature and char yield of Cz-3Th and Cz-4Th CMPs.

СМР	T _{d5%} (°C)	Char yield (%)
Cz-3Th CMP	531	77.5
Cz-4Th CMP	512	79.5

S8. Characterizations of Cz-3Th CMP-St and Cz-4Th CMP-St



Fig. S13 TGA analysis (a) and FE-SEM images (b,c) of Cz-3Th CMP-St and Cz-4Th CMP-St. The char yields of Cz-3Th CMP-St and Cz-4Th CMP-St were 71.8 and 79.8% respectively. The BET surface areas of Cz-3Th CMP-St and Cz-4Th CMP-St were measured to be 156 and 218 m² g⁻¹ respectively.

S9. Hydrogen evolution profiles

Photocatalytic experimental

The photocatalytic experiments were carried out in a 35 mL Pyrex reactor. The reactor was closed using rubber septum's. In a typical photocatalytic reaction, polymers powder was dispersed in 10 mL of the mixture of water/methanol with sacrificial electron donor. The suspension was purged with argon for 5 min to remove dissolved air. After that, the samples were irradiated by a 350 W Xenon lamp equipped with a cut-off filter (1000 W/m², λ : 380-780 nm), and the reaction temperature was kept fixed at 25 °C using flowing cooling water. The formation of hydrogen was confirmed by injecting 0.5 µL of the reactor headspace gas in a Shimazhu gas chromatograph (GC2014) operating at isothermal conditions using a semi-capillary column equipped with a thermal conductivity detector.

Quantum efficiency measurements

In the AQY experiments, the catalyst solution was prepared by dispersing polymers powder in 10 mL of the mixture of water/methanol with sacrificial electron donor. The suspension was illuminated with a 300 W Xe lamp with (Bandpass Filter, 420±2 nm Center, 10±2 nm FWHM). The formation of hydrogen was quantified using a Shimazhu gas chromatograph (GC2014) operating at isothermal conditions using a semi-capillary column equipped with a thermal conductivity detector. The AQY was calculated as follow:

AQY = [(Number of evolved hydrogen molecules × 2) / Number of incident photons] × 100%

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{2 \times M \times N_A}{\frac{E_{total}}{E_{photon}}} \times 100\%$$

$$=\frac{2M \times N_A}{\frac{S \times P \times t}{h \times \frac{c}{\lambda}}} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where, M is the amount of H₂ molecules (mol), NA is Avogadro constant (6.022×10²³/mol), h is the Planck constant (6.626×10⁻³⁴ J·s), c is the speed of light (3×10⁸ m/s), S is the irradiation area (cm²), P is the intensity of irradiation light (W/cm²), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

Table S2. Photophysical properties and Hydrogen Evolution Rate of the polymers

Polymer	HOMO/LUMO (eV) ^a	Bandgap (eV) ^b	HER (µmol h ⁻¹)	AQY (%) ^c	Pd (wt%) d
Cz-3Th-CMP	-5.32/-2.61	2.71	1719.5	1.78	0.86
Cz-4Th-CMP	-5.36/-2.42	2.94	211.9	0.17	1.07

^aHOMO determined by photoelectron spectrometry; ^bLUMO derived by extracting the $E_{HOMO} - E_g$; ^cCalculated using Tauc plot from the absorption onsets; ^eThe AQY is measured at 420 nm; ^d) 1mg of samples were digested using a small amount of hydrogen peroxide with concentrated sulfuric acid. The resulting solutions were run on the inductively coupled plasma optical emission spectrometry (ICP-OES) instrument calibrated with palladium standards at 340 nm.



Fig. S14 Tauc plots calculated from the UV–Vis spectra of Cz-3Th and Cz-4Th CMPs.



Fig. S15 Studied HOMO of Cz-3Th CMP photocatalysts via photoelectron spectroscopy (Model: AC-II)



Fig. S16 Studied HOMO of Cz-4Th CMP photocatalysts via photoelectron spectroscopy (Model: AC-II)



Fig. S17 Determination of photocatalytic activities for Cz-3Th CMP using various sacrificial agents.



Fig. S18 Determination of photocatalytic activities for Cz-4Th CMP using various sacrificial agents.



Fig. S19 Stability test of Cz-4Th CMP as a photocatalyst under visible-light irradiation.



Fig. S20 Electron orbital distributions of the molecular orbitals and dihedral angle of Cz-3Th and Cz-4Th CMPs.



Fig. S21 Impact of Pt concentration on the hydrogen production efficacy of Cz-3Th CMP.



Fig. S22 Impact of Pt concentration on the hydrogen production efficacy of Cz-4Th CMP.



Fig. S23 Photocatalyst amount influence on the hydrogen production activity of Cz-3Th CMP.



Fig. S24 Photocatalyst amount influence on the hydrogen production activity of Cz-4Th CMP.



Fig. S25 Apparent quantum yield of Cz-3Th and Cz-4Th CMPs at 420 nm.



Fig. S26a Control experiment of Cz-3Th CMP.



Fig. S26b Control experiment of Cz-4Th CMP.



Fig. S27 FT-IR spectra of Cz-3Th and Cz-4Th CMPs before and after photocatalytic reaction.



Fig. S28 Solid state ¹³C NMR of Cz-3Th and Cz-4Th CMPs before and after photocatalytic reaction.

Polymer	Conditions	Stability (h)	References
DPP-bdy-TPA	H ₂ O/MeOH/TEOA	36	Macromolecules 53 (2020) 2454-2463.
P1	H ₂ O/TEOA	15	Appl. Cat. B 257 (2019) 117935.
PCTF-1	H ₂ O/TEOA	20	ACS Appl. Mater. Interfaces 10 (2018) 41415-41421.
S-doped g-C ₃ N ₄	H ₂ O/MeOH	8	Mater. Res. Bull. 48 (2013) 3919-3925.
MTCN-6	H ₂ O/TEOA	15	Appl. Cat. B 238 (2018) 592- 598.
PCP4e	H ₂ O/TEA	9	J. Am. Chem. Soc. 138 (2016) 7681-7686.
MIL-125-NH ₂	MeCN/TEA/H ₂ O	12	ACS Appl. Mater. Interfaces 10 (2018) 30035-30039.
CTF-2	H ₂ O/MeOH/TEA	38	Polymer 126 (201 7) 283-290.
CTFS ₁₀	H ₂ O/TEOA	20	J. Mater. Chem. A 4 (2016) 12402-12406.
3SCN-10PCN	H ₂ O/TEOA	12	J. Mater. Sci. 54 (2019) 4811- 4820.
P1	H ₂ O/TEOA	12.5	J. Mater. Chem. C 8 (2020) 8887.
P10	H ₂ O/MeOH/TEA	40	Nat. Commun. 9 (2018) 1-11.
CNBS	H ₂ O/TEOA	20	ACS Appl. Energy Mater. 1 (2018) 5936-5947.
CP-CMP10	H ₂ O/DEA	24	J. Am. Chem. Soc. 137 (2015) 3265-3270.
CdS/g-C ₃ N ₄	H ₂ O/MeOH	28	J. Phys. Chem. C 116 (2012) 13708-13714.
HMP-1	H ₂ O/TEOA	20	Macromol. Rapid Commun. 34 (2013) 1008-1013.
Cz-3Th CMP	H ₂ O/MeOH/TEA	> 300	This work
Cz-4Th CMP	H ₂ O/MeOH/0.1M AA	12	This work

Table S3. Compared the photocatalytic stability of various photocatalysts in the previous literature.

S10. References

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