Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

COMMUNICATION

Tunable Linear Donor-π-Acceptor Conjugated Polymers with Vinylene Linkage for Visible-Light Driven Hydrogen Evolution

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Experimental Section

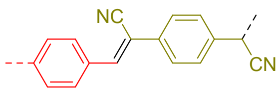
Materials

1,4-phenylenediacetonitrile (NMR, 98%) was supplied by Saan Chemical Technology (Shanghai) Co., Ltd. L-ascorbic acid (AR, >99.0%), 1,3,5-trimethylbenzene (98%, anhydrous grade), 1,4-dioxane (99.5%, anhydrous grade), Polyvinylpyrrolidone (K-30, MW=40000), were supplied by Aladdin Co., Ltd. 1,4-phthalaldehyde (99.7%), 2,5-dimethoxybenzene-1,4-dicarbaldehyde (98.8%), Biphenyl-4,4'-dicarbaldehyde (99.5%), 2,2'-bipyridine-5,5'-dicarboxaldehyde (99.0%) and 2,5-dibromo-1,4-dicarbaldehyde (98.5%) were supplied by Jilin China Science and Technology Co., Ltd. Chloroplatinic acid hexahydrate (AR, 99%), Ethylene glycol (AR, ≥99.0%), acetone (AR, ≥98%), Dichloromethane (AR, ≥99.5%), Tetrahydrofuran (AR, ≥99.5%), Sodium hydroxide (AR, >96.0%), hydrochloric acid (AR, 36.0%~38.0%) and Ethanol (AR, 99.7%) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd.

Material Characterizations

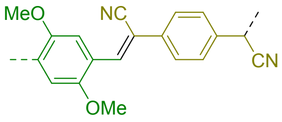
SEM images were taken with a Hitachi S-5800 system. TEM imaging was performed on Tecnai F 20. UV-Vis DRS spectra were measured on a Varian Cary 500 Scan UV-Vis-NIS spectrophotometer using $BaSO_4$ as a reference ranging from 200 to 800 nm. XRD measurements were performed on a Bruker D8 Advance X-ray diffractometer equipped with a Cu $K_{\alpha1}$ radiation (λ = 1.5406 Å). FT-IR spectra were collected on a Bruker Vertex 70 V FT-IR spectrometer. Solid state ^{13}C CP-MAS NMR measurements were carried out on Bruker Avance III/WB solid-state NMR spectrometer operating at 400 MHz equipped with a standard 4 mm magic angle spinning double resonance probe head. Fluorescence emission spectrum of the sample was measured by a fluorescence spectrometer of the Japanese Hitachi F 4600 model. Transient absorption spectra of the samples were tested using a HORIBA DeltaPro spectrometer. TGA analysis was conducted on Mettler Toledo TGA/DSC1 thermal analyzer under N_2 with the temperature raising from 25 °C to 800 °C at a rate of 10 °C min^{-1}. Elemental analysis was conducted on an Elementar vario MICRO cube. The DFT simulation was performed on Dmol3 module of Materials Studio suite of programs.

Preparation of CFP



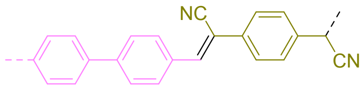
A 10 mL Schlenk tube was charged with 1,4-phthalaldehyde (PF) (8.6 mg, 0.064 mmol), PDAN (10.0 mg, 0.064 mmol), mesitylene/1,4-dioxane (0.75 ml, 1/5 by vol.) and aqueous NaOH solution (0.1 ml, 0.1 M), and the mixture was sonicated for two minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120 °C for three days. The mixture was cooled to room temperature and the precipitate was collected by centrifugation, washed with H_2O, acetone, THF and DCM for several times, respectively. Soxhlet extracted in THF for two days and dried under vacuum at 100 °C for 12 h to afford red precipitation in 88.5% isolated yield. Elemental analysis: expected C (85.02%), H (3.96%), N (11.02%) and measured C (77.86%), H (4.71%), N (8.86%).

Preparation of CBOP



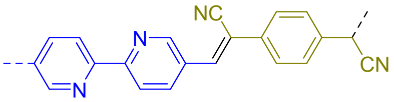
A 10 mL Schlenk tube was charged with 2,5-dimethoxybenzene-1,4-dicarbaldehyde (BOF) (12.4 mg, 0.064 mmol), PDAN (10.00 mg, 0.064 mmol), mesitylene/1,4-dioxane (0.75 ml, 1/5 by vol.) and aqueous NaOH solution (0.1 ml, 0.1 M), and the mixture was sonicated for two minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120 °C for three days. The mixture was cooled to room temperature and the precipitate was collected by centrifugation, washed with H_2O, acetone, THF and DCM for several times, respectively. Soxhlet extracted in THF for two days and dried under vacuum at 100 °C for 12 h to afford red precipitation in 80.7% isolated yield. Elemental analysis: expected C (84.48%), H (5.67%), N (9.85%) and measured C (88.96%), H (4.77%), N (7.84%).

Preparation of CBBP



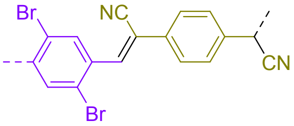
A 10 mL Schlenk tube was charged with Biphenyl-4,4'-dicarbaldehyde (BBF) (13.4 mg, 0.064 mmol), PDAN (10.00 mg, 0.064 mmol), mesitylene/1,4-dioxane (0.75 ml, 1/5 by vol.) and aqueous NaOH solution (0.1 ml, 0.1 M), and the mixture was sonicated for two minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120 °C for three days. The mixture was cooled to room temperature and the precipitate was collected by centrifugation, washed with H_2O, acetone, THF and DCM for several times, respectively. Soxhlet extracted in THF for two days and dried under vacuum at 100 °C for 12 h to afford red precipitation in 83.4% isolated yield. Elemental analysis: expected C (87.25%), H (4.27%), N (8.48%) and measured C (82.58%), H (4.70%), N (7.30%).

Preparation of CBPP



A 10 mL Schlenk tube was charged with 2,2'-bipyridine-5,5'-dicarboxaldehyde (BPF) (13.6 mg, 0.064 mmol), PDAN (10.00 mg, 0.064 mmol), mesitylene/1,4-dioxane (0.75 ml, 1/5 by vol.) and aqueous NaOH solution (0.1 ml, 0.1 M), and the mixture was sonicated for two minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120 °C for three days. The mixture was cooled to room temperature and the precipitate was collected by centrifugation, washed with H_2O, acetone, THF and DCM for several times, respectively. Soxhlet extracted in THF for two days and dried under vacuum at 100 °C for 12 h to afford red precipitation in 87.1% isolated yield. Elemental analysis: expected C (79.50%), H (3.64%), N (16.86%) and measured C (71.20%), H (4.33%), N (14.42%).

Preparation of CBRP



A 10 mL Schlenk tube was charged with 2,5-dibromo-1,4-dicarbaldehyde (BRF) (18.7 mg, 0.064 mmol), PDAN (10.00 mg, 0.064 mmol), mesitylene/1,4-dioxane (0.75 ml, 1/5 by vol.) and aqueous NaOH solution (0.1 ml, 0.1 M), and the mixture was sonicated for two minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120 °C for three days. The mixture was cooled to room temperature and the precipitate was collected by centrifugation, washed with H_2O, acetone, THF and DCM for several times, respectively. Soxhlet extracted in THF for two days and dried under vacuum at 100 °C for 12 h to afford red precipitation in 84.0% isolated yield. Elemental analysis: expected C (52.19%), H (1.95%), N (6.76%) and measured C (45.11%), H (2.02%), N (5.35%).

Preparation of PVP-Pt colloid

According to the previous report by our group[1], in a 50 ml Schlenk tube, 0.11 g of poly (N-vinyl-2-pyrrolidone) (PVP, MW 40 000) and 0.50 ml of an aqueous solution of $H_2PtCl_6\cdot 6\cdot H_2O$ (5.0 mg/ml) were dissolved in 24 ml of ethylene glycol. Then 1 ml of an ethylene glycol solution of 0.20 M NaOH was added dropwise. After just 30 s of microwave irradiation at the maximum power output of 750 W, the solution changed from orange to black and a PVP-stabilized Pt colloid was obtained.
The maximum content of Pt load (W) is estimated the following equation:

$$\begin{aligned}W(Pt) &= (C(H_2PtCl_6)\times M(Pt)\times V(H_2PtCl_6))/(M(H_2PtCl_6)\times m(cat.))\times 100\% \\ &= (5.00\times 195.078\times 0.5)/(409.81\times 10)\times 100\% \\ &= 11.90\%\end{aligned}$$

where C(Pt) is the maximum concentration of Pt load, $C(H_2PtCl_6)$ is the concentration of H_2PtCl_6, $M(H_2PtCl_6)$ is the molar mass of H_2PtCl_6, M(Pt) is the molar mass of Pt, C(Pt) is the maximum concentration of Pt load, $V(H_2PtCl_6)$ is the volume of H_2PtCl_6, m(cat.) is the mass of polymer catalyst.

Photoelectrochemical Measurements

Photocatalyst powder was ultrasonically dispersed in ethanol. The solution was then dropcast onto fluorine-doped tine oxide (FTO) conductive glass with an exposed area of 0.5×0.5 cm^2. The conventional three-electrode electrochemical cells were equipped with a working electrode, a platinum foil counter electrode and an Ag/AgCl (3.0 M KCl) electrode as the reference electrode. The electrode potential was converted to the reversible hydrogen electrode (RHE) potential according to the Nernst equation.

$$E_{RHE} = E_{Ag/AgCl} + 0.059\,pH + E°_{Ag/AgCl}$$

Where E_{RHE} is the converted potential versus RHE, $E°_{Ag/AgCl} = 0.2$ V at 25℃, and $E_{Ag/AgCl}$ is the measured potential versus the Ag/AgCl reference. The working electrode was the as-prepared FTO conductive glass. 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte.
The Mott-Schottky analysis was conducted by Zahner workstation in the dark at the frequency of 500, 1000 and 1500 Hz.
EIS analysis was performed at the open circuit condition at the frequency range from 0.1 to 100000 Hz.

Photocatalytic H_2 Evolution

Photocatalyst powder (10 mg) was first dispersed in 75 ml of H_2O with the addition 5.11 mmol of L-ascorbic acid in an online photocatalytic hydrogen production system (Labsolar-6A, PerfectLight of Beijing). The dispersion was ultrasonicated for 5 minutes. A 25ml of PVP-Pt colloid was introduced as the precursor to Pt cocatalyst deposition on surface. The solution was then carefully evacuated to remove the air and filled with Ar. For photocatalytic experiments, the solution was directly irradiated by a 300 W Xe-lamp with a cutoff filter (λ > 420 nm). The reaction temperature was maintained at 5.5 °C by a water-cooling system. The amount of H_2 was determined using an on-line gas chromatograph (TCD, molecular sieve 5Å, Ar carrier, GC-8A).

Apparent Quantum Yield (AQY)

A 300 W Xe-lamp with monochromatic light (λ = 420 nm, 450 nm, 480 nm, 520nm and 550 nm) was used as the light source for performing the AQY calculation. The light intensity was determined by an optical power meter. AQY for H_2 production was estimated according to the following equation:

$$\begin{aligned}AQY\ (\%) &= 2\times\ H_2 \text{ amount / number of incident photons} \\ &= 2\times (n_{H2}\cdot N_A\cdot h\cdot c) / (I\cdot S\cdot t\cdot \lambda) \times 100\%\end{aligned}$$

where n_{H2} is the hydrogen evolution mole numbers of 100 mg material in irradiation times, N_A is the Avogadro constant (6.022×10^{23} mol^{-1}), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light (3×10^{8} m s^{-1}), S is the irradiation area (cm^{2}), I is the light intensity (W cm^{-2}), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

Fourier Transform Infrared (FTIR) Spectroscopy

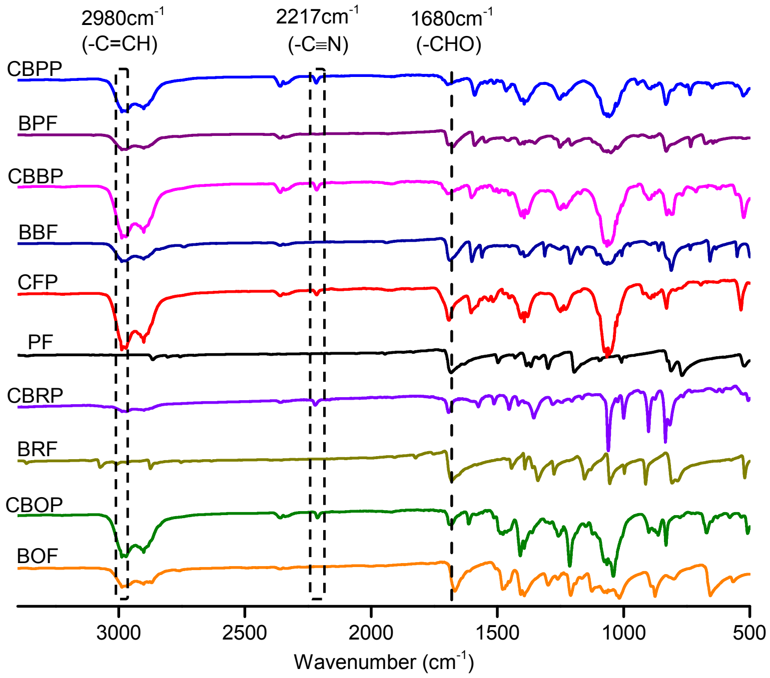


Figure S1. FT-IR spectra of the as-synthesized linear polymers and the corresponding monomer

Solid-State ^{13}C NMR Spectroscopy

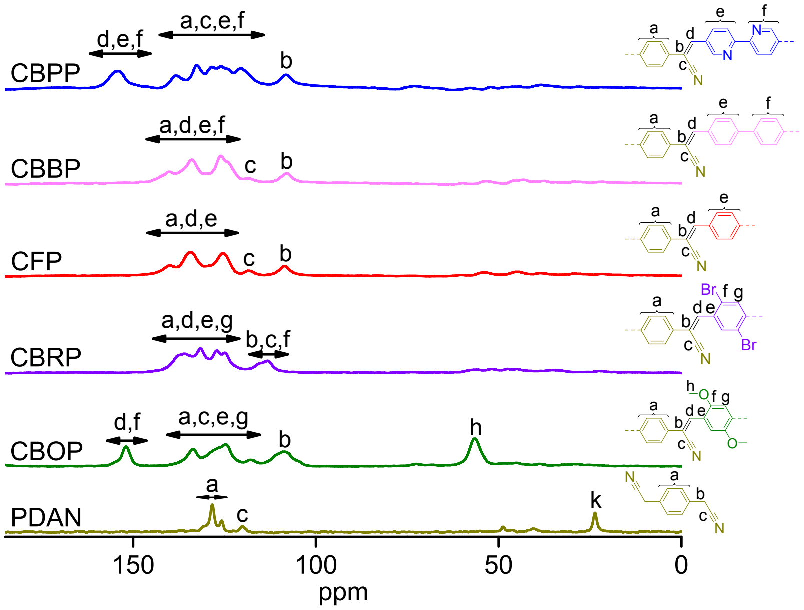


Figure S2. Solid-state ^{13}C NMR spectrum of PDAN, CBPP, CBBP, CFP, CBRP

Thermogravimetric Analysis

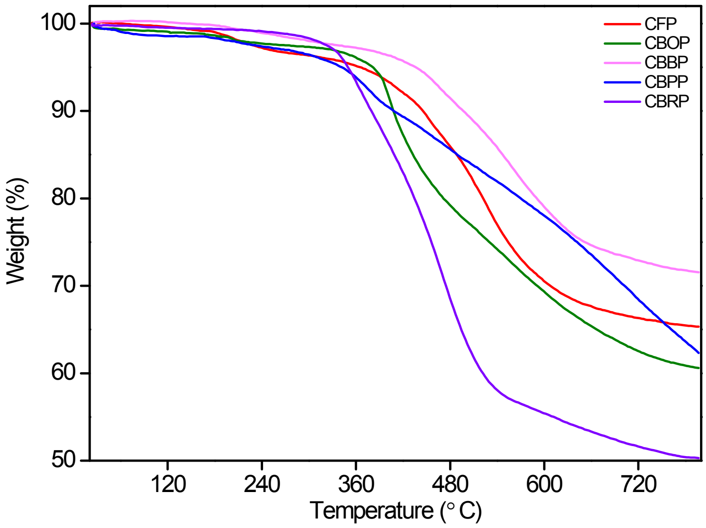


Figure S3. The thermogravimetric analysis plots of CFP, CBOP, CBBP, CBPP and CBRP under N_2 with the

Scanning Electron Microscopy (SEM) and Transmission Electron Microscope (TEM) Characterization

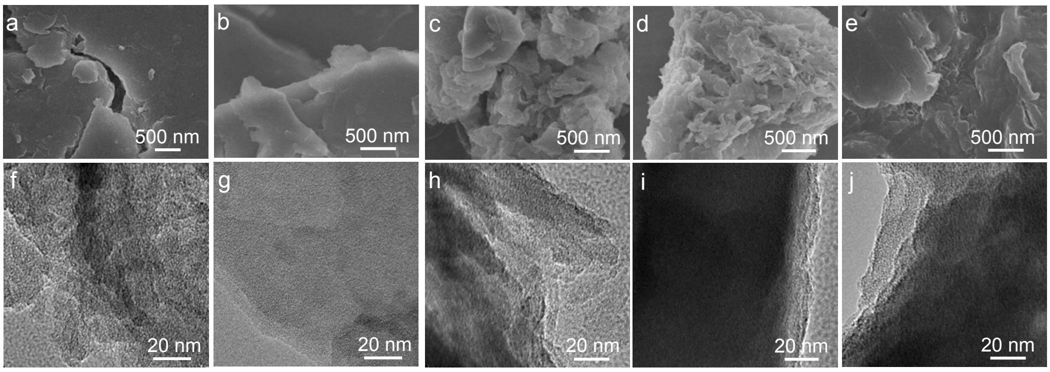


Figure S4. SEM images of as-synthesized CBPP (a), CBBP (b), CFP (c), CBOP (d) and CBRP (e). TEM images of

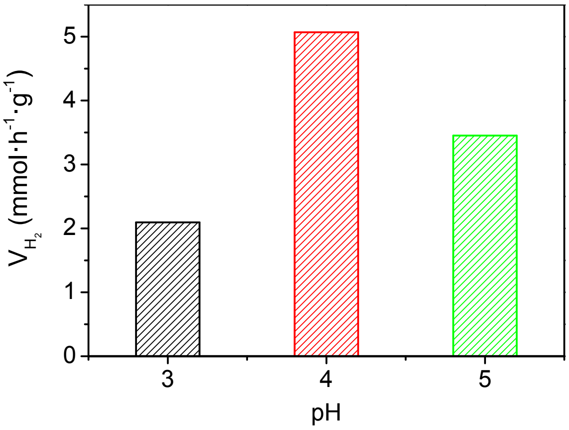


Figure S5. The photocatalytic hydrogen evolution rate (HER) of CFP, using PVP-Pt as co-catalysts in the presence of ascorbic acid (H_2A) as an electron donor during the initial 3 h under visible light irradiation (λ≥400 nm) at various pH values.

Stability Characterization

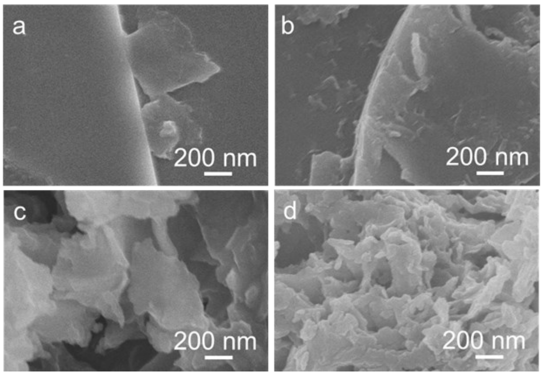


Figure S6. SEM images of corresponding linear polymers after photocatalysis: a) CBPP, b) CBBP, c) CFP and d) CBRP.

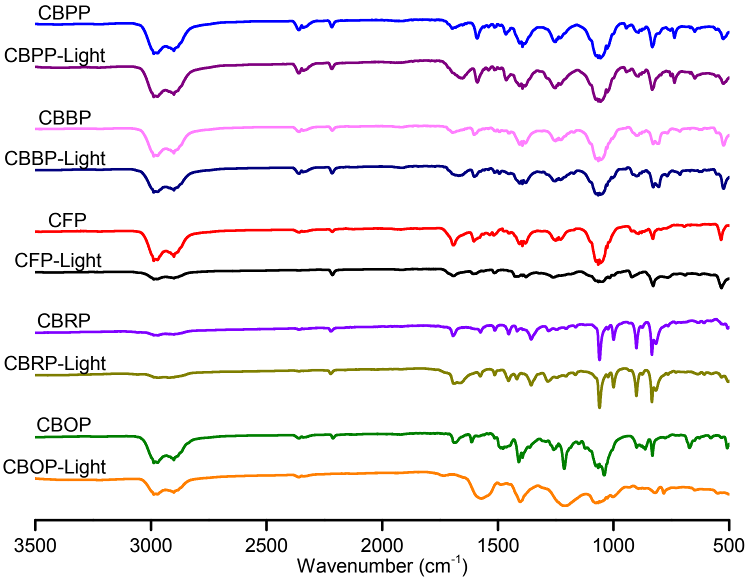


Figure S7. FT-IR spectra of corresponding linear polymers before and after photocatalytic reaction.

Control Experiments of Photocatalytic Hydrogen Production

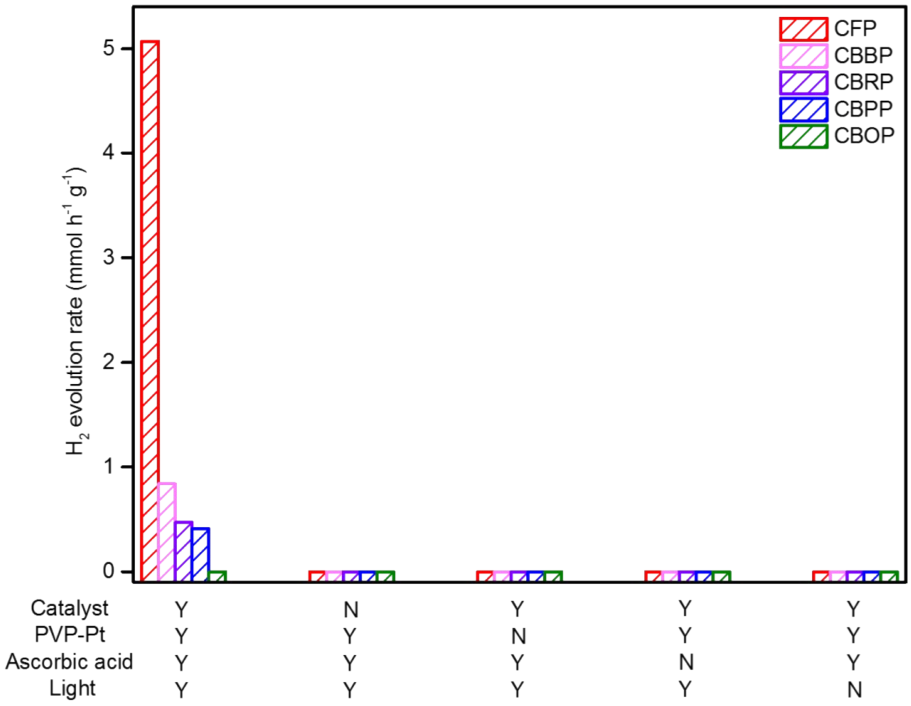


Figure S8. Photocatalytic H_2 production rates of as-synthesized polymers in the photocatalytic systems under visible light irradiation ($\lambda \geq 420$ nm). The control experiments showed that no or only negligible hydrogen evolution was observed in the absence of any component (polymer, PVP-Pt H_2A or light). (Y: existence, N: absence.)

Fluorescence Emission Spectra

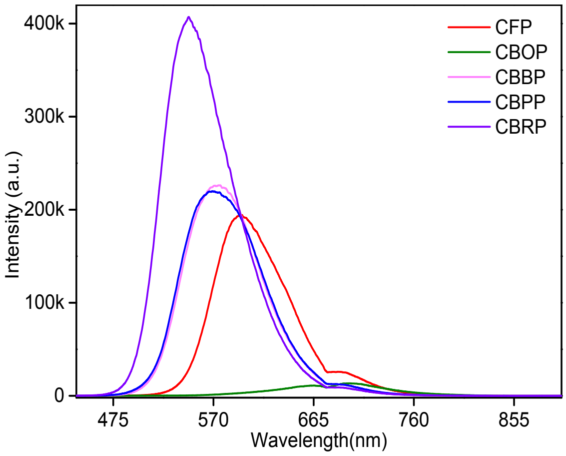


Figure S9. Solid-state fluorescence emission spectra of the as-synthesized polymers (λ_{ex} = 360

Elemental analysis

Table S1. Elemental analysis results of CFP, CBOP, CBBP, CBPP and CBRP. The deviation of experimental values from the nominal stoichiometry is due to the absorption of H_2O. However, the relative molar ratio of C/N is reasonably consistent with the expectation.

Samples	**Expected (%)**				**Measured (%)**			
	C	N	H	C/N	C	N	H	C/N
CFP	85.02	11.02	3.96	7.72	77.80	8.86	4.71	8.78
CBOP	84.48	9.85	5.67	8.58	71.38	7.84	4.77	9.10
CBBP	87.25	8.48	4.27	10.29	82.58	7.30	4.70	11.31
CBPP	79.5	16.86	3.64	4.72	71.20	14.42	4.33	4.94
CBRP	52.19	6.76	1.95	7.72	45.11	5.35	2.02	8.42

DFT calculation:

Table S2. a, b) the LUMO and HOMO orbital levels of the model segment of the corresponding monomer aromatic aldehyde. c) The torsion model segment (the yellow labeled atom construct torsion plane) of the

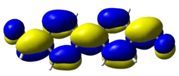
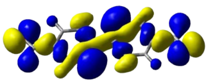
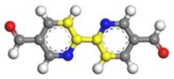
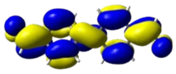
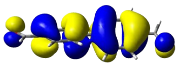
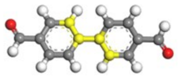
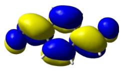
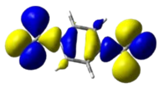
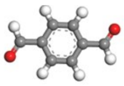
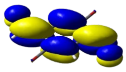
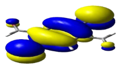
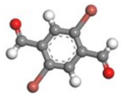
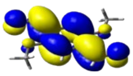
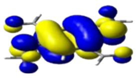
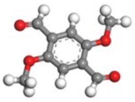
	a	b	c
BPF			
BBF			
PF			
BRF			
BOF			

Table S3. a) the HOMO orbital level of the model segment of the corresponding dimer, b) The torsion model segment (the yellow labeled atom construct torsion plane) of the corresponding dimer, c) The torsion model segment of the corresponding trimer (z plane).

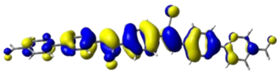
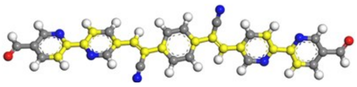
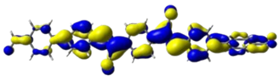
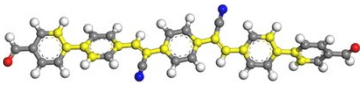
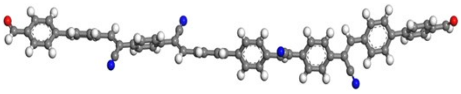
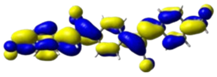
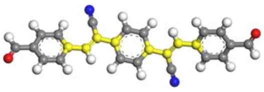
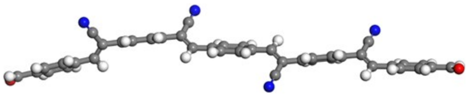
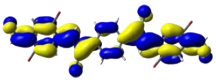
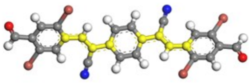
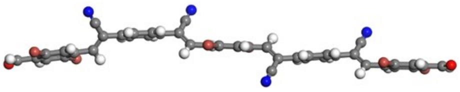
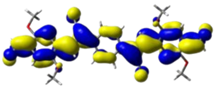
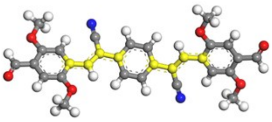
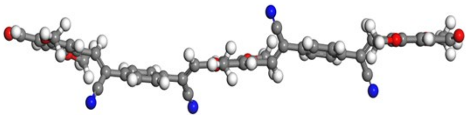
	a	b	c
CBPP			
CBBP			
CFP			
CBRP			
CBOP			

Table S4. DFT calculation summary for materials.

	HOMO (ev)	LUMO (ev)	HOMO-LUMO gap (ev)	Dimer Torsional angles A [°]	Dimer Torsional angles B [°]
BPF	3.02	-1.20	4.22	0.005	/
BBF	2.84	-1.70	4.54	37.493	/
PF	3.16	-1.40	4.56	0	/
BRF	3.18	-1.02	4.20	0	/
BOF	1.94	-1.77	3.71	0	/
CBPP dimer	2.32	-0.88	3.20	0.017 / 0.070	0.774 / 0.872
CBBP dimer	2.06	-1.26	3.32	39.413 / 39.943	0.8181 / 1.818
CFP dimer	2.40	-0.95	3.35	0 / 0	0.884 / 0.890
CBRP dimer	2.60	-0.62	3.22	0 / 0	1.622 / 1.640
CBOP dimer	1.72	-1.21	2.93	0 / 0	1.032 / 1.033

[A]: the dihedral angle between the central ring and the peripheral phenyl rings.
[B]: the dihedral angle between the phenyl ring from 1,4 - phenylene diacetonitrile and the peripheral phenyl ring from C2-symmetric aromatic core.

AQY:

Table S5 The AQY and its corresponding parameters for calculation at different wavelenght.

λ (nm)	**S (cm^{-2})**	**t (h)**	**I (mw/cm^2)**	**$n_{(H2)}$ (mmol)**	**AQY(%)**
420	40.72	10	15.5	5.2	1.3
435	40.72	10	24.0	6.9	1.1
450	40.72	10	12.7	3.6	0.99
500	40.72	3	7.40	0.48	0.71
550	40.72	10	5.00	0.20	0.12

Table S6. Parameters obtained from fitting kinetic traces of time-resolved fluorescence for the linear D-π-A polymers in **Figure 3a** in the main text.

polymer	τ_1 (*ns*)	τ_1 (%)	τ_2 (*ns*)	τ_2 (%)	τ_1 (ns)
CBPP	0.43	73	5.01	27	1.67
CBBP	0.39	83	4.87	17	1.15
CFP	0.39	78	6.33	22	1.70
CBRP	0.39	50	0.39	50	0.39
CBOP	0.30	93	4.04	7	0.56

References

1. H. Lin, D. Liu, J. Long, Z. Zhang, H. Zhuang, Y. Zheng, X. Wang, *Phys. Chem. Chem. Phys.* 2015, **17**, 10726-10736.