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Electronic Supplementary Information

Improving the photocatalytic performance of conjugated polyelectrolytes via substituent optimization

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Content

1. Experimental section

Materials: All chemicals without special explanation were brought from Shanghai Richjoint Chemical Co., Ltd. 5-Fluorobenzo-[2,1,3]-thiadiazole, 5-chlorobenzo-2,1,3-thiadiazole were purchased from Beijing Warwick Chemical Co., Ltd. Diethylamine, bromoethane, sodium hydride, $Pd(PPh_3)_4$, $Pd_2(dba)_3$, trimethyltin chloride, extra dry methanol (99.8%), anhydrous tetrahydrofuran, HPLC chlorobenzene, and HPLC toluene were purchased from Energy Chemical and used with no more treatment. n-Butyl lithium was brought from J&K Scientific Co., Ltd. 4,8-bis((6-bromohexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (M1) [1.2] and 6,6'-(2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-9,9-diyl)bis(N,N-diethylhexan-1-amine) (M7) [3] were synthesized referencing the published literatures.

6,6'-(benzo[1,2-b:4,5-b']dithiophene-4,8-diylbis(oxy))bis(N,N-diethylhexan-1-amine) (M2)

M1 (5.45 g, 10 mmol) dissolved in 60 mL of DMF was put into flask, and then diethylamine (15 mL) was added. The reaction mixture was refluxed under nitrogen overnight. Next day, the reaction mixture was poured into ice water and then extracted with dichloromethane. The organic phase was then washed by water for three times, dried with anhydrous $MgSO_4$, and evaporated under vacuum to obtain the crude product. After purifying by column chromatography with petroleum ether/dichloromethane/triethylamine (10: 4: 1) as eluent, the pure product (M2) was obtained as canary yellow oil with a yield of 60%.

^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 7.47-7.46 (d, 2H), 7.37-7.35(d, 2H), 4.29-4.26 (t, 4H), 2.56-2.52 (m, 8H), 2.46-2.43 (t, 4H), 1.91-1.85 (m, 4H), 1.63-1.57 (m, 4H), 1.55-1.49 (m, 4H), 1.42-1.38 (m, 4H), 1.05-1.02 (t, 12H).

^{13}C-NMR (126 MHz, $CDCl_3$, δ, ppm): 144.49, 131.58, 130.15, 126.00, 120.29, 77.31, 77.06, 76.81, 73.84, 52.90, 46.87, 30.50, 27.52, 26.96, 26.08, 11.64.

6,6'-((2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(oxy))bis(N,N-diethylhexan-1-amine) (M3)

M2 (2.58 g, 3 mmol) and 50 mL of THF were added into a flask under argon. 2.5 M n-BuLi (4.8 mL, 12 mmol) was added dropwise into the solution at -78 °C. After being stirred for 1 h, a great deal of white solid precipitate appeared in the flask. Then, 1 M trimethyltin chloride (12 mL, 12 mmol) was injected by syringe at -78 °C. Stirred for 1 h, the reaction was allowed to warm to room temperature, and the reactant turned clear rapidly. The reaction was stirred at ambient temperature overnight. Then, it was poured into 150 mL of cool water and extracted by dichloromethane three times. The organic layer was washed with water two times and then dried by anhydrous $MgSO_4$. After removing solvent under vacuum, the residue was recrystallized from acetonitrile two times. M3 was obtained as brown crystals (2.2 g, yield 86%).

^{1}H-NMR (500 MHz, MeOD, δ, ppm): 7.49 (s, 2H), 4.30-4.27 (t, 4H), 2.56-2.51 (m, 8H), 2.47-2.43 (t, 4H), 1.88-1.81 (m, 4H), 1.67-1.59 (m, 4H), 1.55-1.48 (m, 4H), 1.42-1.37 (m, 4H), 1.04-1.0 (t, 12H), 0.50-0.35 (m, 18H).

^{13}C-NMR (126 MHz, MeOD, δ, ppm): 142.78, 141.28, 134.02, 132.84, 127.30, 73.07, 52.26, 46.31, 30.09, 27.11, 25.83, 25.58, 9.74, 9.93.

4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (M4)

5-Fluorobenzo-[2,1,3]-thiadiazole (6.82 g, 40 mmol) and 40% hydrobromic acid solution 60 mL were put into a two-necked flask. The reaction mixture was refluxed under nitrogen for 1 h. Then 10.4 mL of Br_2 (31.96 g, 200 mmol) was added drop by drop, and the reaction mixture was refluxed for additional 48 hours. After cooled to room temperature, the reaction mixture was poured into saturated solution of sodium thiosulfate to quench the excess liquid bromine, then extracted with dichloromethane. The organic phase was washed by water for three times, dried with anhydrous $MgSO_4$, and evaporated under vacuum to obtain the crude product. After purifying by column chromatography with petroleum ether/dichloromethane (2: 1) as eluent, the product was further recrystallized from petroleum ether. M4 was obtained as white solid. (7.48 g, yield 60%).

^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 7.78-7.80 (d, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$, δ, ppm): 160.91, 159.22, 152.73, 150.26, 123.93, 113.99, 98.25.

4,7-dibromo-5-methoxybenzo[c][1,2,5]thiadiazole (M5)

NaH（360 mg, 15 mmol）was added to a 100 mL dry two-necked flask. After degassed for 3 times, 50 mL of anhydrous tetrahydrofuran and extra dry methanol (4.8 g, 150 mmol) were added to reaction mixture, and stirred at 50 °C for 3 h. Then M2 (3.12 g, 10 mmol) was added to the mixture and stirred under nitrogen at 50 °C overnight. After cooled to room temperature, the reaction mixture was poured into deionized water, then extracted with dichloromethane. The organic phase was washed by water for three times, dried with anhydrous $MgSO_4$, and evaporated under vacuum to obtain the crude product. After purifying by column chromatography with petroleum ether/dichloromethane (4: 1) as eluent, the pure product (M5) was obtained as canary yellow solid with a yield of 60%.

^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 7.75 (s, 1H), 4.10 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$, δ, ppm): 157.16, 153.53, 149.00, 121.55, 113.60, 98.79, 58.01.

4,7-dibromo-5-chlorobenzo[c][1,2,5]thiadiazole (M6)

5-chlorobenzo-2,1,3-thiadiazole (3.41 g, 20 mmol) and 40% hydrobromic acid solution 40 mL was put into a two-necked flask. The reaction mixture was refluxed under nitrogen for 1 h. Then 5.2 mL of Br_2 (15.98 g, 100 mmol) was added drop by drop, and the reaction mixture was refluxed for additional 48 hours. After cooled to room temperature, the reaction mixture was poured into saturated solution of sodium thiosulfate to quench the excess liquid bromine, then extracted with dichloromethane. The organic phase was then washed by water for three times, dried with anhydrous $MgSO_4$, and evaporated under vacuum to obtain the crude product. After purifying by column chromatography with petroleum ether/dichloromethane (2: 1) as eluent, the product was further recrystallized from petroleum ether M4 was obtained as white solid. (4.07 g, yield 62%).

^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 7.78-7.80 (d, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$, δ, ppm): 160.91, 159.22, 152.73, 150.26, 123.93, 113.99, 98.25.

Synthetic Procedure for PFB series Polymers

PFB-F, PFB-Cl and PFB-OMe were synthesized by a standard Pd-catalyzed Suzuki polymerization. Typically, 0.2 mmol of M4 (M5, M6) and M7 (0.2 mmol) were placed in a 15 mL pressure bottle, then HPLC chlorobenzene (2 mL), THF (1 mL) and Cs_2CO_3 (2.0 M aqueous solution, 1 mL) were added. The mixture was then degassed for three times to remove the oxygen. Then $Pd(PPh_3)_4$ (1 mg) was added, and the mixture was degassed once again and then heated to 110 ℃ for 12 h to get the polymers PFB-F, PFB-Cl and PFB-OMe. The polymer solution was then precipitated into methanol and the solid was collected and dried. Then, the crude product was redissolved by chloroform. The chloroform solution was concentrated and precipitated into methanol again. The solid was collected and dried under vacuum for 12 h to yield the polymer.

PFB-F: yellow solid, yield (114 mg, 87%) ^{1}HNMR (500 MHz, $CDCl_3$, δ, ppm): 8.11-7.81 (m, 7H), 2.49-

2.42 (m, 8H), 2.35 -2.27 (m, 4H), 2.13-2.04 (d, 4H), 1.32-1.17 (m, 12H), 1.04-0.91 (m, 16H). GPC ($CHCl_3$), M_n=26.1 kDa, $Đ$=1.73.

PFB-Cl: tan solid, yield (108 mg, 80%) ^{1}HNMR (500 MHz, $CDCl_3$, δ, ppm): 8.08-7.70 (m, 7H), 2.52-2.45 (m, 8H), 2.33-2.32(d, 4H), 2.07(s, 4H), 1.41-1.25 (t, 4H), 1.16(s, 8H), 1.01-0.94 (m, 16H). GPC ($CHCl_3$), *Mn*=22.7 kDa, $Đ$=2.47.

PFB-OMe: tan solid, yield (122 mg, 91%) ^{1}HNMR (500 MHz, $CDCl_3$, δ, ppm): 8.07-7.81 (m, 7H), 4.07-4.06 (d, 3H), 2.51-2.43 (m, 8H), 2.37-2.31 (m, 4H), 2.08 (s, 4H), 1.35 (s, 4H), 1.25-1.18 (d, 8H), 1.0-0.94 (m, 16H). GPC ($CHCl_3$), M_n=13.1 kDa, $Đ$=2.02.

Synthetic Procedure for PBB series Polymers

PBB-F, PBB-Cl and PBB-OMe were synthesized by a Pd-catalyzed Stille polymerization. Typically, 0.1 mmol of M4 (M5, M6) and M3 (0.1 mmol) were placed in a 15 mL pressure bottle, then HPLC chlorobenzene (1 mL) and DMF (2 mL) were added. The mixture was then degassed for three times to remove the oxygen. Then $Pd_2(dba)_3$ (1 mg) and $P(o\text{-}tol)_3$ (2 mg) were added, and the mixture was degassed once again and then heated to 110 ℃ for 12 h to get the polymers PBB-F, PBB-Cl and PBB-OMe. The polymer solution was then precipitated into methanol and the solid was collected and dried. Then, the crude product was redissolved by chloroform. The chloroform solution was concentrated and precipitated into methanol again. The solid was collected and dried under vacuum for 12 h to yield the polymer.

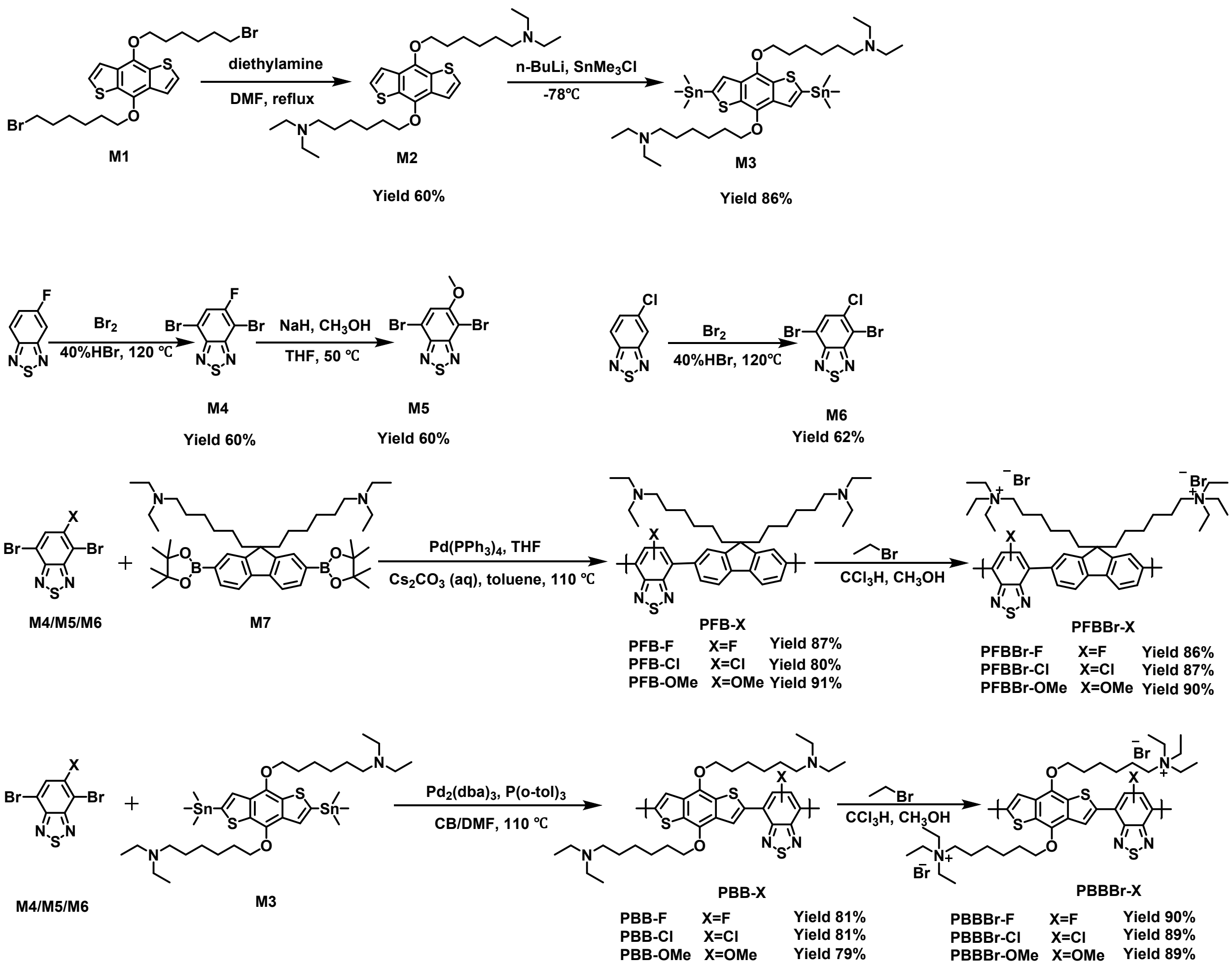
PBB-F: blue solid, yield (58 mg, 81%) ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 4.21(s, 4H), 3.06-2.57 (m, 12H), 1.89-1.10 (m, 28H). GPC ($CHCl_3$), *Mn*=28.3 KDa, $Đ$=1.74.

PBB-Cl: blue solid, yield (58 mg, 81%) ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 8.79-8.71(d, 1H), 8.15-7.90 (t, 2H), 4.41 (s, 4H), 2.75(s, 8H), 1.98-1.5 (t, 24H), 1.25-1.16 (t, 8H). GPC ($CHCl_3$), *Mn*=20.6 kDa, *Đ*=2.89.

PBB-OMe: blue solid, yield (57.2 mg, 79%) ^{1}H-NMR (500 MHz, $CDCl_3$, δ, PPM): 4.32 (s, 4H), 4.07-4.00 (d, 3H), 2.79(s, 12H), 1.16-2.79 (m, 28H). GPC ($CHCl_3$), *Mn*=22.0 KDa, *Đ*=2.66

Synthesis of PFBBr-F, PFBBr-Cl, PFBBr-OMe, PBBBr-F, PBBBr-Cl and PBBBr-OMe

Donor-acceptor linear conjugated polyelectrolytes were synthesized from their corresponding neutral polymeric precursors. Typically, 0.1 mmol of polymeric precursor (PFB-F, PFB-Cl, PFB-OMe, PBB-F, PBB-Cl and PBB-OMe) was dissolved in 20 mL of chloroform with 2 mL of bromoethane and the mixture was stirred at 50 ℃ for 5 days. During the reaction, 2 mL of methanol was added every 8 h. Then the polymer solution was concentrated and precipitated into a mixture of hexane and ethyl acetate (3:1). The solid was collected and dried. Then, the crude product was redissolved by methanol. The methanol solution was then concentrated and precipitated into a mixture of hexane and ethyl acetate (3:1) again. The final polyelectrolyte was then collected and dried. PFBBr-F: yellow solid, yield (75 mg, 86%), PFBBr-Cl: tan solid, yield (78 mg, 87%), PFBBr-OMe: tan solid, yield (78 mg, 90%), PBBBr-F: blue solid, yield (84 mg, 90%), PBBBr-Cl: blue solid, yield (82 mg, 89%), PBBBr-OMe: blue solid, yield (84 mg, 89%).



Scheme S1. Synthetic procedures of monomers and conjugated polyelectrolytes

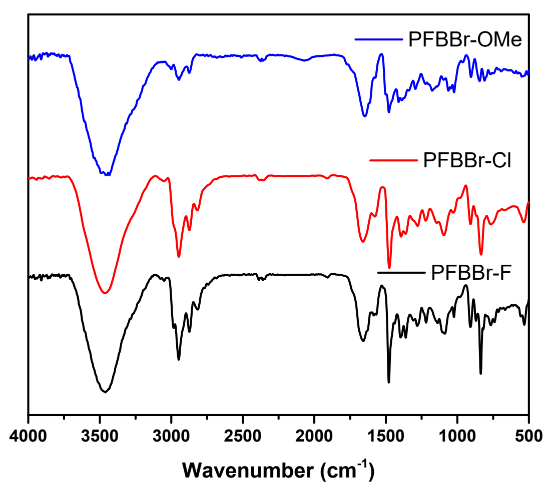


Figure S1 The fourier transform infrared spectroscopy of PFBBr series CPEs

2. Characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy spectra of monomers and polymers were recorded by Bruker AVANCE Digital NMR workstation operating at 600 and 150 MHz, respectively. Molecular weights of these polymers were measured by Waters GPC 2410 with a refractive index (RI) detector and using a calibration curve with polystyrene standards where $CHCl_3$ was used as mobile phase. UV-vis spectra of the polymers were tested by HP 8453 spectrophotometer. Cyclic Voltammetry (CV) measurements were carried out on a CHI660E electrochemical workstation under argon atomosphere. The saturated calomel electrode (SCE) was used as reference electrode, a platinum wire electrode was used as counter electrode and glassy carbon electrode was used as working electrode. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) dissolved in anhydrous acetonitrile was used as the supporting electrolyte for the measurement. Electrochemical impedance spectroscopys were also tested by CHI660E electrochemical workstation with Ag/AgCl electrode as reference electrode, platinum wire electrode as counter electrode, indium tin oxide electrode as working electrode and Na_2SO_4 in aqueous solution (0.1 M) as supporting electrolyte. UPS measurements were performed on the Thermo ESCALAB 250XI. The valance band (*VB)* spectra were measured with a monochromatic He I light source (21.2 eV) and a VG Scienta R4000 analyzer. A sample bias of -5 V was applied to observe the secondary electron cutoff. The photoluminescence spectra and temperature-dependent photoluminescence spectra range from 120K to 300K, excited at a wavelength of 420 nm, were recorded by an FLS920 spectrofluorimeter. The femtosecond transient absorption spectroscopy (fs-TAS) of these polymers and their kinetics were measured with a ms2004i transpec SP transient absorption photometer.

3. Measurement of Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution experiment was performed on the Labsolar-IIIAG Photo-catalytic Online Analysis System (Beijing Perfectlight) with a top-irradiation reaction vessel. In details, 2.5 mg of CPEs dissolved in methanol (0.5 mL) was dispersed into 50 mL of aqueous solution with ascorbic acid (0.2M, PH=4 adjusted by 1.0 M NaOH solution). After sonication for 30 min, Pt (from H_2PtCl_4) of each CPE was added and illuminated for 0.5 h to form Pt nanopaticles as cocatalysts. The calculated weight of Pt cocatalysts is 3% of that of each polyelectrolyte. The reaction unit was sealed with a quartz septum and the resulted reaction mixture was degassed by vacuuming to remove the dissolved oxygen and methanol. A Xe lamp (300W, Ceaulight) was used as the light source. The luminous power reaching the surface of the reaction solution was calibrated to be 150 mW cm^{-2} by a power meter. And the hydrogen was recorded by gas chromatography (GC7900II, using Ar as carrier gas). The sensor was standardized by injecting different volumes of hydrogen with the experiment condition. The sensor was polarized at +36 mV until reaching a stable value before every measurement.

4. The Cartesian Coordinates of Six Model Systems Optimized at the Theoretical Level of M06-2X/6-311G(d)

FB-F

	X	Y	Z
C	-5.02255900	-0.86584800	0.34497700
C	-6.07525300	-0.06230200	-0.10970500
C	-5.78080700	1.17577300	-0.68470000
C	-4.46959300	1.62586700	-0.81464900
C	-3.43630700	0.81791200	-0.35916800
C	-3.71685300	-0.42801700	0.22026400
C	-1.98107900	1.01125000	-0.35639600
C	-1.38711300	-0.11652900	0.22497700
C	-2.43732000	-1.13429000	0.63977100
C	-1.19208000	2.06045700	-0.81410000
C	0.18775600	1.97169000	-0.68233500
C	0.79067500	0.84772100	-0.10155400
C	-0.01418000	-0.20603900	0.35312500
C	-2.40740500	-1.38342800	2.15335300
C	-2.25467100	-2.45390300	-0.12249300

C	-7.49880900	-0.53829200	0.02510200
C	2.26083800	0.76630500	0.02803400
C	3.04761500	1.81435800	0.40738000
C	4.46801300	1.77839800	0.54524900
C	5.18710300	0.65046900	0.30180400
C	4.42996100	-0.49667100	-0.10344600
C	2.99260200	-0.44548000	-0.23567700
N	4.94529900	-1.68395400	-0.39689400
S	3.70509500	-2.64734700	-0.80719400
N	2.47380600	-1.60283900	-0.62905600
C	6.67481700	0.55241900	0.42989000
F	2.48726100	2.99854900	0.69927300
H	-5.24222200	-1.83208700	0.79400400
H	-6.59578000	1.79966300	-1.03787600
H	-4.26662700	2.59216600	-1.26470900
H	-1.63798700	2.93679200	-1.27245700
H	0.81142400	2.78026000	-1.04307900
H	0.44552400	-1.08115100	0.79835600
H	-3.20915300	-2.06674800	2.44534600
H	-1.45580200	-1.83277700	2.44894200
H	-2.53319500	-0.44935200	2.70390100
H	-3.04654900	-3.16074600	0.13909100
H	-2.28374200	-2.28622000	-1.20059100
H	-1.29336000	-2.91047200	0.12702200
H	-8.20351200	0.19306600	-0.37212200
H	-7.65153900	-1.47735300	-0.51273100
H	-7.75583000	-0.71712300	1.07217800

H	4.95116900	2.69623200	0.86224300
H	7.10613900	1.50051900	0.75031900
H	6.94593300	-0.22176500	1.15123000
H	7.12240900	0.26432900	-0.52396300

FB-Cl

	X	Y	Z
C	-5.11959900	-0.79949800	-0.48354100
C	-6.14660100	-0.09743900	0.15542300
C	-5.81646700	0.97865800	0.98481600
C	-4.49578600	1.36660900	1.18367300
C	-3.48635300	0.66105800	0.53965500
C	-3.80183500	-0.42091500	-0.29224000
C	-2.02718700	0.82418300	0.55333100
C	-1.46659500	-0.15853800	-0.27329400
C	-2.54447800	-1.04270800	-0.87893200
C	-1.21141800	1.73122400	1.22018600
C	0.16439200	1.65197900	1.04364900
C	0.73098300	0.67840700	0.21403500
C	-0.09724000	-0.24056900	-0.44143600
C	-2.38004200	-2.49908000	-0.42286500
C	-2.54187600	-0.95886400	-2.41088200
C	-7.58749300	-0.47619700	-0.07117300
C	2.19996300	0.58817800	0.05207600
C	3.02419600	1.61477500	-0.31859400

C	4.44901600	1.49463800	-0.45042100
C	5.11064600	0.32956900	-0.22049700
C	4.30114400	-0.78789800	0.16166000
C	2.87194200	-0.66305000	0.29298900
N	4.75200300	-2.00753500	0.42796600
S	3.45831700	-2.91113900	0.81265800
N	2.28679800	-1.79866500	0.65784300
C	6.59294100	0.16412300	-0.34777500
Cl	2.37598700	3.18289400	-0.72289300
H	-5.36519800	-1.64144300	-1.12666400
H	-6.61298800	1.52095900	1.48491200
H	-4.26478600	2.20401200	1.83397200
H	-1.63308700	2.48877800	1.87211700
H	0.81454400	2.34512800	1.56496500
H	0.34317600	-1.00628000	-1.07184600
H	-1.43469100	-2.91003900	-0.78651600
H	-2.38609000	-2.56748500	0.66638700
H	-3.19294100	-3.11713600	-0.81306700
H	-1.60467300	-1.35059200	-2.81467900
H	-3.36237600	-1.54830200	-2.82836400
H	-2.65531000	0.07424700	-2.74430000
H	-8.21078400	-0.19954100	0.78056200
H	-7.98913800	0.03218900	-0.95243500
H	-7.69520400	-1.54992000	-0.23452400
H	4.99717700	2.37966100	-0.75249600
H	7.06901500	1.09584100	-0.65249300
H	7.02417300	-0.15914300	0.60233900

H	6.82921900	-0.61037700	-1.08094500

FB-OMe

	X	Y	Z
C	-5.16488500	-0.77711100	-0.44915500
C	-6.19169200	-0.00719300	0.10965900
C	-5.85763100	1.13052800	0.84789300
C	-4.53273900	1.51436700	1.03603300
C	-3.52469600	0.74199500	0.47359900
C	-3.84529800	-0.40386200	-0.26829600
C	-2.06338100	0.88303000	0.49820500
C	-1.50585800	-0.17500800	-0.23017500
C	-2.58825000	-1.09170000	-0.77729500
C	-1.23974700	1.83165200	1.09408400
C	0.13684800	1.71329500	0.95055600
C	0.70535300	0.65844200	0.22395000
C	-0.13570100	-0.29385700	-0.36775100
C	-2.45423700	-2.50614300	-0.19650200
C	-2.55970900	-1.13959100	-2.31039200
C	-7.63217800	-0.39477700	-0.10545300
C	2.17432000	0.52579400	0.09522000
C	3.00776600	1.57988800	-0.21211200
C	4.43311600	1.42720700	-0.33863100
C	5.07182900	0.23656400	-0.16997200
C	4.24733700	-0.88503100	0.14896800

C	2.81774300	-0.74197300	0.27899100
N	4.68289600	-2.12207000	0.35881100
S	3.37660800	-3.02402300	0.69572400
N	2.21937500	-1.89033800	0.58861400
C	6.55310100	0.05593900	-0.29341800
O	2.42423000	2.79145200	-0.39573900
C	3.18589800	3.86476800	-0.90728500
H	-5.41453700	-1.66756900	-1.02199700
H	-6.65272800	1.72656900	1.28504100
H	-4.29872700	2.40122500	1.61597800
H	-1.65733200	2.65285100	1.66739800
H	0.78928200	2.44423800	1.41090100
H	0.29564000	-1.11754500	-0.92594500
H	-3.26793500	-3.14533500	-0.54966000
H	-1.50708500	-2.95733500	-0.50335600
H	-2.48248200	-2.48121100	0.89427300
H	-3.38172900	-1.75154100	-2.69125500
H	-2.65221100	-0.13706800	-2.73221000
H	-1.62147800	-1.57647900	-2.66217700
H	-8.29303200	0.12429300	0.59002600
H	-7.95638900	-0.14573200	-1.11980900
H	-7.77760100	-1.46873700	0.02903900
H	5.03094500	2.29773400	-0.57858500
H	7.04729000	0.99423900	-0.54604300
H	6.97144800	-0.32242700	0.64209700
H	6.78551000	-0.68392600	-1.06275700
H	2.47805700	4.67445800	-1.06638100

H	3.95035700	4.19186300	-0.19664500
H	3.65541600	3.60370800	-1.85989300

BB-F

	X	Y	Z
C	-5.85848100	-0.39119100	0.04858800
S	-5.21453700	1.18665900	-0.38174200
C	-3.57906600	0.60603300	-0.18525800
C	-3.55880200	-0.76180600	0.18220800
C	-4.88996800	-1.29616500	0.31189600
C	-2.42071800	1.34265500	-0.36024700
C	-1.19606800	0.69627800	-0.15714000
C	-1.17364000	-0.66712700	0.21300300
C	-2.33793500	-1.40495200	0.38292600
C	0.12415100	1.23396500	-0.28339400
C	1.10405400	0.32640900	-0.01289100
S	0.45087000	-1.26274200	0.39516200
O	-2.28579800	-2.72621600	0.74049300
C	-2.27507100	-3.60202800	-0.38287500
O	-2.47516100	2.66165300	-0.72043300
C	-2.39770100	3.54510200	0.39499300
C	2.54647300	0.57183300	0.01022900
C	3.09495100	1.81688900	0.16351300
C	4.48865700	2.11159400	0.19889700
C	5.43707100	1.14294900	0.08936200

C	4.94348800	-0.19239900	-0.06342600
C	3.52862800	-0.47631600	-0.10314500
N	5.70068700	-1.27611000	-0.17820600
S	4.69728100	-2.54276800	-0.32046500
N	3.27164300	-1.76889700	-0.24622600
C	6.91123600	1.39465200	0.12249000
C	-7.33950000	-0.59228200	0.08676100
F	2.29972300	2.88745400	0.30267200
H	-5.09291900	-2.31769900	0.60857400
H	0.31372600	2.25395400	-0.58187100
H	-2.22117300	-4.61417400	0.01297700
H	-3.18835200	-3.48285700	-0.97337000
H	-1.40608800	-3.40793300	-1.01783000
H	-2.46424600	4.55493000	-0.00452800
H	-3.22567100	3.36554700	1.08651800
H	-1.44902700	3.41845900	0.92463300
H	4.76013800	3.15396300	0.32487100
H	7.12742000	2.45477500	0.25208700
H	7.37530100	0.83573500	0.93819200
H	7.37844800	1.04846800	-0.80222500
H	-7.56861600	-1.61867700	0.37450800
H	-7.81254800	0.07876600	0.80746300
H	-7.79090900	-0.40172100	-0.88973100

BB-Cl

	X	Y	Z
C	-5.92052400	-0.36421500	-0.02445300
S	-5.21754700	1.06686700	-0.76389300
C	-3.60782900	0.51546200	-0.37150400
C	-3.63896900	-0.73602200	0.29097900
C	-4.98825600	-1.20488500	0.47589700
C	-2.42370900	1.17426600	-0.65387100
C	-1.22651000	0.56877000	-0.25861900
C	-1.25573400	-0.67813900	0.40750100
C	-2.44521500	-1.33875800	0.68605500
C	0.11430200	1.04297200	-0.43794600
C	1.04846500	0.20430700	0.07550500
S	0.34495700	-1.23593500	0.80125100
O	-2.44136800	-2.54613300	1.33222300
C	-2.40958900	-3.65244600	0.43495900
O	-2.42699500	2.38241400	-1.29607000
C	-2.36392300	3.48747200	-0.39830000
C	2.50083900	0.41130300	0.10130100
C	3.11614200	1.57291400	0.49048800
C	4.53894400	1.75975700	0.49702400
C	5.41057400	0.78491100	0.12480200
C	4.82740300	-0.45753800	-0.28136700
C	3.39978100	-0.64317200	-0.29317300
N	5.50179700	-1.52935100	-0.67842700
S	4.40262700	-2.66989200	-1.03433800
N	3.04010500	-1.85273600	-0.70420100
C	6.89867700	0.94299900	0.12399800

C	-7.40687500	-0.52510900	-0.00819600
Cl	2.20046300	2.93834800	1.06677400
H	-5.23059200	-2.13083700	0.98243800
H	0.35628800	1.96599500	-0.94744400
H	-2.39519100	-4.55015500	1.04969100
H	-3.29685700	-3.65524900	-0.20503800
H	-1.51298200	-3.61895900	-0.19027400
H	-2.38220500	4.38605300	-1.01147600
H	-3.22315600	3.48330000	0.27821100
H	-1.44098300	3.45790700	0.18871200
H	4.91084800	2.72388300	0.82375000
H	7.18998900	1.93910200	0.45608700
H	7.36094500	0.20168600	0.77968600
H	7.29961800	0.77187100	-0.87754000
H	-7.67496200	-1.45857900	0.48729400
H	-7.88881300	0.29660000	0.52660300
H	-7.81476700	-0.54590800	-1.02150100

BB-OMe

	X	Y	Z
C	-5.96224900	-0.40300500	-0.19676500
S	-5.27547600	1.18689600	-0.50003500
C	-3.65675200	0.55483300	-0.32047000
C	-3.67402700	-0.83329600	-0.03998500
C	-5.01882500	-1.34590300	0.01960700

C	-2.47851100	1.27192400	-0.42912400
C	-1.27181600	0.58299100	-0.26234200
C	-1.28666000	-0.79952200	0.02691300
C	-2.47149500	-1.51605900	0.13901600
C	0.06148600	1.09600100	-0.34310800
C	1.02359600	0.15507400	-0.12123400
S	0.32179800	-1.44763900	0.15879400
O	-2.46063500	-2.85853800	0.41402300
C	-2.48816600	-3.13715000	1.80932900
O	-2.49987400	2.61559500	-0.69628200
C	-2.36737500	3.41303300	0.47475900
C	2.47450900	0.35430200	-0.06919200
C	3.06203600	1.58485300	0.17812000
C	4.48644800	1.76592500	0.23973800
C	5.37992300	0.75275700	0.07219300
C	4.82470500	-0.53831300	-0.17345400
C	3.39757100	-0.73298400	-0.24525500
N	5.52582500	-1.65114800	-0.35381200
S	4.45513200	-2.84599200	-0.59153000
N	3.07492600	-2.00025900	-0.47817800
C	6.86536000	0.92561400	0.13042000
C	-7.44701800	-0.57706600	-0.22293500
O	2.23795600	2.64404900	0.35894800
C	2.76009500	3.88064800	0.80286400
H	-5.24782300	-2.38913100	0.19870400
H	0.27877200	2.12499600	-0.57854100
H	-2.46719800	-4.22044500	1.91101900

Polyelectrolytes	PFB-F	PFB-Cl	PFB-OMe	PBB-F	PBB-Cl	PBB-OMe
E_{ox} [V]	1.41	1.69	1.21	0.56	0.56	0.37
E_{re} [V]	-1.03	-1.11	-1.28	-0.93	-0.88	-0.98
HOMO (eV)	-5.58	-6.13	-5.65	-5.00	-5.00	-4.81
LUMO (eV)	-3.41	-3.32	-3.16	-3.51	-3.56	-3.47

H	-1.61720300	-2.70414800	2.30949300
H	-3.40109400	-2.73995600	2.26356600
H	-2.41157500	4.45106900	0.15050700
H	-3.18388600	3.21039500	1.17390500
H	-1.41098800	3.21913100	0.97022500
H	4.87284900	2.76007700	0.42470700
H	7.13658800	1.96260600	0.32876900
H	7.29294300	0.29269000	0.91138700
H	7.32338300	0.61459100	-0.81124200
H	-7.70327500	-1.61724600	-0.01979900
H	-7.93462700	0.04847300	0.52852200
H	-7.86029100	-0.30740200	-1.19767700
H	1.89478900	4.51606800	0.97548700
H	3.31636400	3.76635200	1.73687300
H	3.39717600	4.34266600	0.04426400

Table S1 The energy level of neutral polymer precursors for CPEs photocatalysts

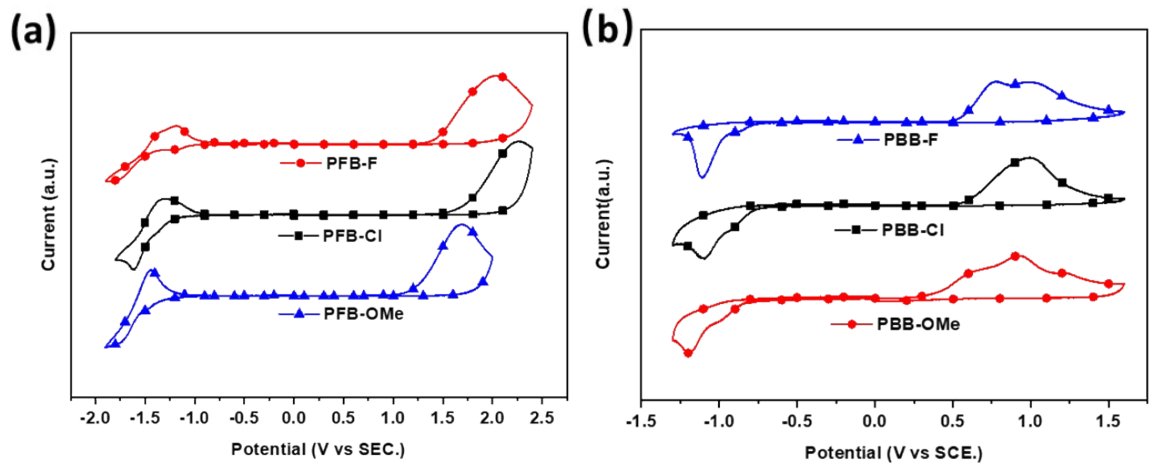


Figure S2 The cyclic voltammetry curves of neutral polymer precursors for CPEs photocatalysts

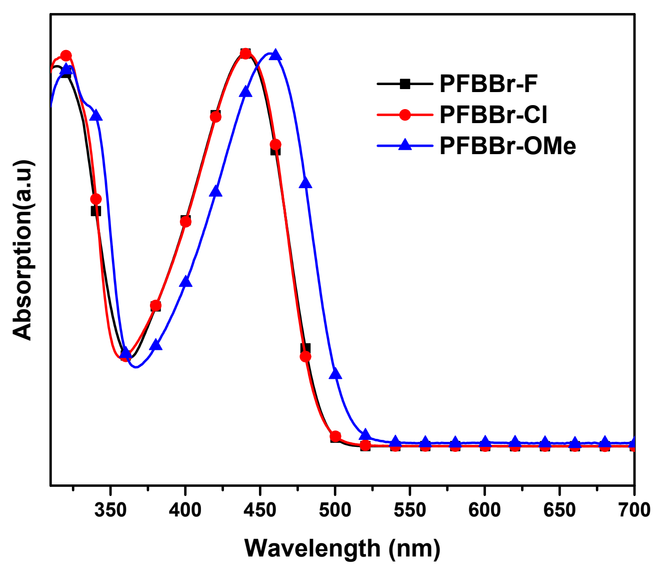


Figure S3 UV-Vis absorption of the PFBBr series of polyelectrolytes in the photocatalytic solution

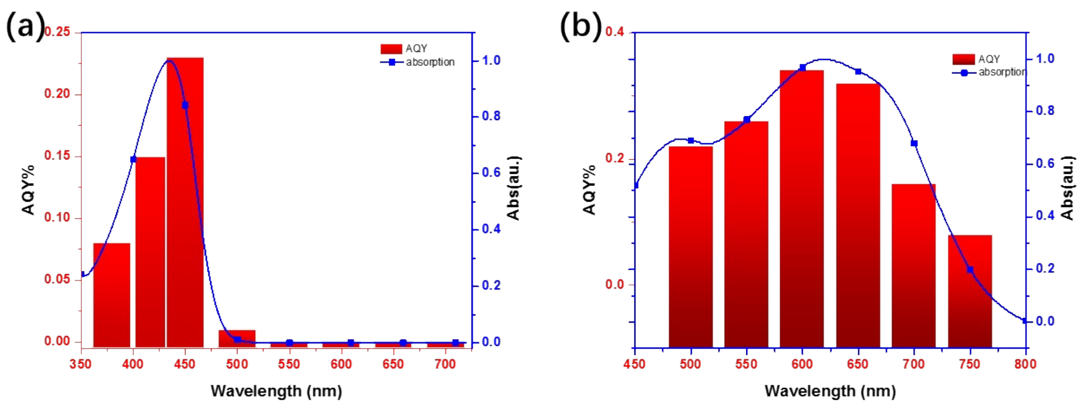


Figure S4 Overlayer of AQY and UV–vis absorption(a), PFBBr-F (b), PBBBr-Cl

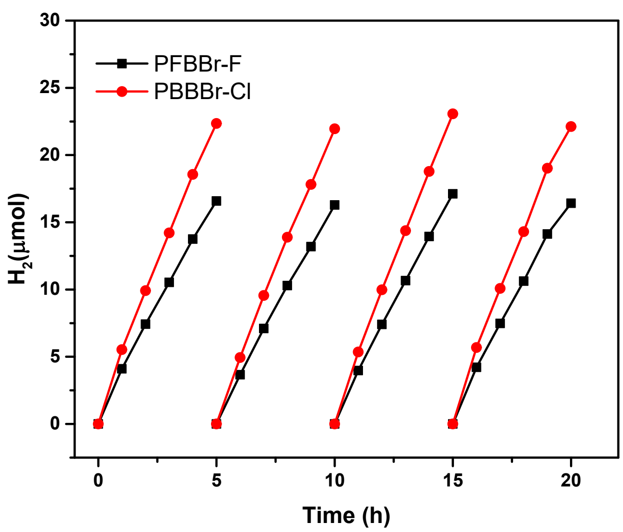


Figure S5 Hydrogen evolution of PFBBr-F and PBBBr-F with over long-time illumination (20 h)

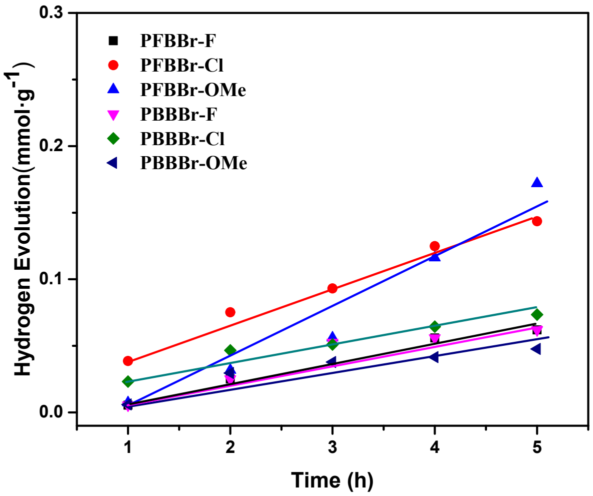


Figure S6 Time courses of hydrogen evolution for these CPEs without Pt cocatalyst

Table S2 the dipole moments of the oligomer models for CPEs

oligomer	FB-F	FB-Cl	FB-OMe	BB-F	BB-Cl	BB-OMe
μ_g (D)	0.680	0.669	3.074	0.983	0.563	5.250
μ_{gx} (D)	0.497	0.112	1.657	0.943	0.544	1.845
μ_{gy} (D)	-0.310	-0.611	2.267	0.266	-0.123	3.392
μ_{gz} (D)	0.344	-0.247	-1.251	0.089	-0.082	3.557
μ_e (D)	9.777	10.606	8.471	13.253	16.026	11.961
μ_{ex} (D)	9.369	10.279	5.881	-13.183	-15.986	-10.042
μ_{ey} (D)	-2.656	2.524	5.842	1.315	0.855	5.157
μ_{ez} (D)	0.876	0.673	1.747	0.360	0.728	3.955

μ_{ge} (D)	9.192	10.680	6.294	14.167	16.578	12.024

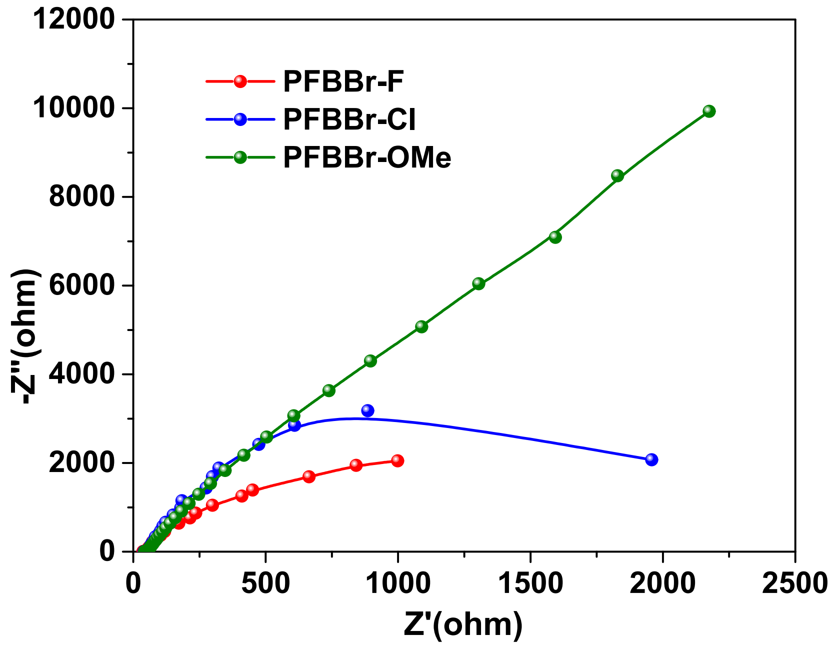


Figure S7. EIS Nyquist plots of conjugated polymers.

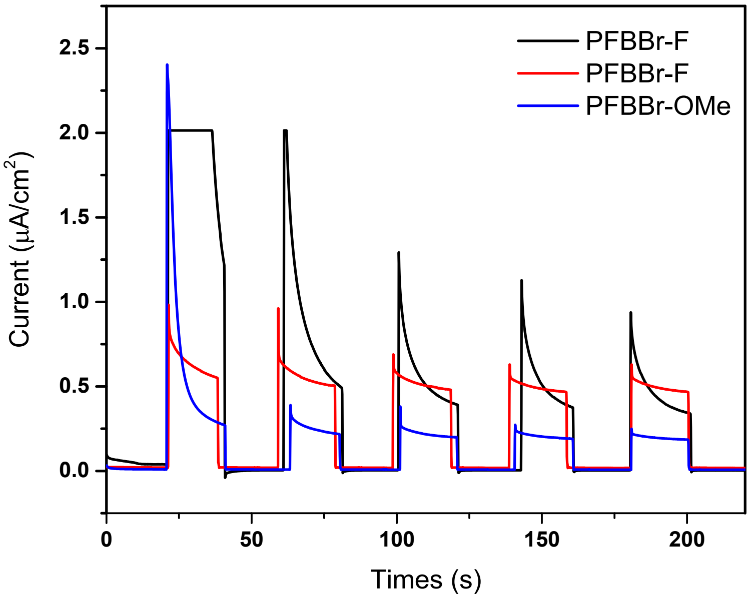


Figure S8 Photocurrent response of the conjugated polymers

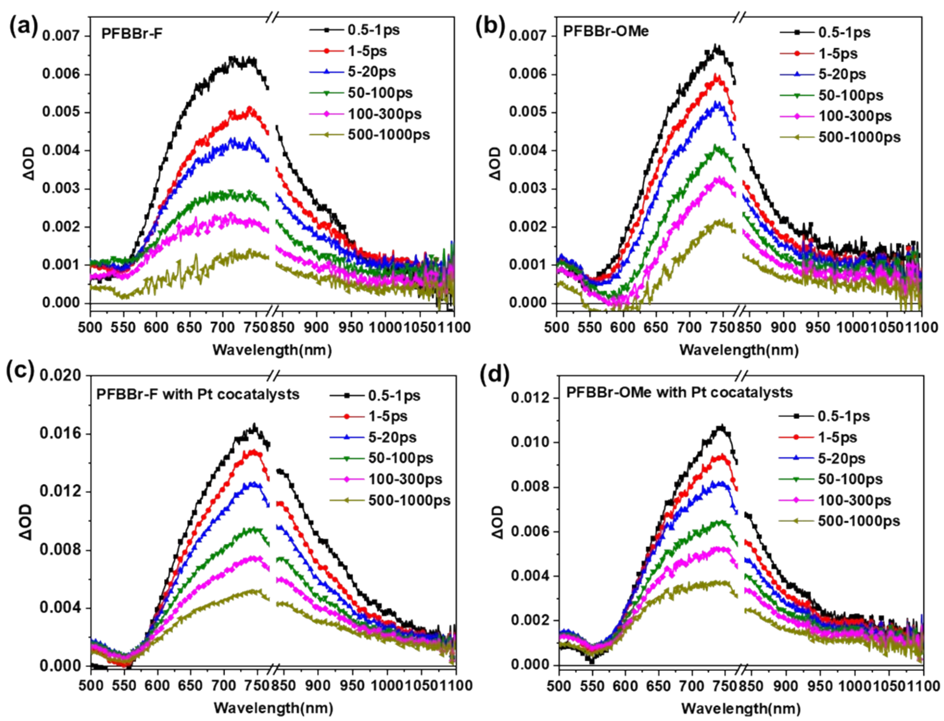


Figure S9. fs-TAS spectra of PFBBr-F (a), PFBBr-OMe (b), PFBBr-F with Pt (c) and PFBBr-OMe with (d)solution in water

Reference:

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(2) T. P. Osedach, T. L. Andrew, V. Bulović, *Energy Environ. Sci*., 2013, **6**, 711-718.
(3) F. Huang, H. Wu, D. Wang, W. Yang, Y. Cao, *Chem. Mater.,* 2004, **16**, 708-716.