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Supporting Information

Comonomer effect

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1. Material and Characterization:

All Chemicals were bought from commercial sources ACROS Organics, Alfa Aesar, Sigma-Aldrich or TCI. Solvents, deuterated solvents and starting materials were used without further purification. Monomers were purified by filtration through basic Aluminium oxide to remove present inhibitors.

Methods:

¹H- and ¹³C-NMR spectra were recorded with a Bruker AVIII 300 spectrometer at 400 MHz and 101 MHz respectively, using DCM- d_2 and DMSO- d_6 and are given in ppm against TMS. NMR Data were analysed using MestReNova 14.2.3. Polymers were analysed via gel permeation chromatography (GPC) using a PSS SECcurity² instrument with RI and UV detector at 270 nm wavelength using a PMMA standard in DMF. Fourier-transform infrared spectroscopy was performed using dry samples incorporated into potassium bromide pellets and measured with a Bruker Vertex 70. Bruker OPUS 7.8 software was used for Data analysis.

Light scattering measurements were performed using a ALV/CGS3 compact goniometer system with a He/Ne laser (632.8 nm). Measurements were performed at 20°C at 9 angles from 30° to 150° using a solution in DMF 2mg/ml and analysed with ALV5000 software

Fluorescence spectroscopy, including quantum yield, Stern Volmer Plot and excitation spectra where measured on a Duetta Fluorescence and Absorbance Spectrometer from Horiba using EzSpec as software for analysis and fluorescence peak integration. UV/Vis-absorption spectra were also measured on a Cary 60 UV–Vis/NIR spectrometer.

Fluorescence lifetime was measured on using a Pico Quant. PDL 800-D, Pico Quant. PH 300 with an LDH-P-C-375 and analysed using PicoHarp V 2.2.0.0 as well as FluoFit Pro. V4.4.0.1 over a time of 10 minutes with a degassed solution in DMF.

For cyclic voltammetry measurements a glassy carbon electrode as the working electrode, $Hg/HgCl_2$ electrode as the reference electrode, and a platinum wire as the counter electrode, were used. The measurements were performed on a Metrohm Autolab PGSTAT204 potentiostat/galvanostat using Nova 2.1 software. The measurements were performed by coating the working electrode with a polymer solution in the present of nafion perfluorinated resin solution in an ACN solution (NH_4PCl_6 5.wt %)

Gas chromatographic mass spectroscopy was performed on a Shimadzu GC-2010 plus combined with a QP2010 ultra mass spectrometer using a 7HG-G010-11 Phenomenex column and helium 5.0 as carrier. Methods were adjusted explicit for the required separation leading to three-used temperature curves.

DFT calculations were performed using Gaussian 16. The DFTs for the HOMO/LUMO levels were calculated for optimization of local minimum using method rb3lyp/6-31+g(d) Frontier molecular orbitals pictures were produced using Avogadro.

Photoreactor LEDs (Tru Components™ HighPower, 1.4 W per LED, λ=460-470 nm power

2. Reactions

2.1 Polymer synthesis:



R: -CN, -CO₂Et, -Ph R₂: -H, -CH₃

The monomer was first purified by basic aluminum oxide. In a dry flask methyl methacrylate or acrylonitrile (500 mg) was combined with 4-phenyl-7-(4-vinylphenyl)benzo[c][1,2,5]thiadiazole (5 wt%. 25 mg) and dissolved in dry DMF (1.5 mL). The solution was degassed by N₂ bubbling for 10 min. AIBN (1 wt.%) was dissolved in DMF (0.5 mL) and degassed by N₂ bubbling. The solutions were combined and heated under stirring at 80 °C overnight. The polymers were precipitated in diethyl ether and centrifuged for 10 min. (4000 rpm. 5 °C). The supernatant was discarded and the polymer taken up in DMF. The precipitation and centrifugation was repeated and the polymer purified via Soxhlet in diethyl ether for two days. The polymer was dried under vacuum and the concentration of incorporated photocatalyst is determined via a UV/Vis-calibration.

The monomer was first purified by basic aluminum oxide. In a dry flask methyl styrene (500 mg) was combined with 4-phenyl-7-(4-vinylphenyl)benzo[c][1,2,5]thiadiazole (5 wt%. 25 mg) and dissolved in dry DMF (1.0 mL). The solution was degassed by N₂ bubbling for 10 min. AIBN (2 wt.%) was dissolved in DMF (0.5 mL) and degassed by N₂ bubbling. The solutions were combined and heated under stirring at 80 °C overnight. The polymers were precipitated in methanol and centrifuged for 10 min. (4000 rpm. 5°C). The supernatant was discarded and the polymer taken up in DMF. The precipitation and centrifugation was repeated and the polymer purified via Soxhlet in methanol for two days, yielding a yellow powder for all samples. The polymer was dried under vacuum and the concentration of incorporated photocatalyst was determined via a UV/Vis-calibration.

2.2 Photocatalytic C-C coupling of 3-methylindol

Diethyl 2-(3-methyl-1H-indol-2-yl)malonate



In a 2 ml flask equipped with a stir bar, 3-methyl indole (19.7 mg, 150 μ mol), diethyl bromomalonate (71.7 mg, 300 μ mol) and triphenylamine (73.6 mg, 300 μ mol) and photocatalytic polymer (250 nmol photoactive unit) were dissolved in DMF (2 mL). The solution was degassed with Argon for 10 minutes and irradiated under blue light (λ =460-470 nm). Samples (100 μ L) were taken, diluted with DCM and directly measured via GCMS.

The reaction was purified via silica column chromatography DCM: PE 1:9 \rightarrow EtAc: PE 8:2

¹H NMR (400 MHz, CD_2CI_2) δ 8.93 (s, 1H), 7.54 (ddt, *J* = 7.9, 1.4, 0.8 Hz, 1H), 7.36 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.18 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 5.00 (s, 1H), 4.35 - 4.10 (m, 4H), 2.30 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H).

 ^{13}C NMR (101 MHz, $CD_2Cl_2)\,\delta$ 167.75, 136.19, 128.66, 125.22, 122.65, 119.55, 119.06, 111.34, 110.84, 62.71, 49.79, 14.21, 8.59.

GC/MS method: Splitless injection, Inject. Temp. 220 °C, Oven Temp: 60 °C hold 2 min., rate 70 °C/min. to 220 °C hold 4 min., rate 70 °C/min. to 280 °C hold 1 min. Pressure 92.4 kPa, total flow 36.5 ml/min.

2.3 Photocatalytic C-C coupling of 4-chlorobenzyl bromide

1,2-bis(4-chlorophenyl)ethane



In a 2 ml flask equipped with a stir bar, 4-chlorobenzyl bromide (20.5 mg, 100 μ mol) *N*,*N*-diisopropylethylamine (175 μ L, 1 mmol) and photocatalytic polymer (300 nmol photocatalytic moiety) were dissolved in DMF (2mL). The solution was degassed with Argon for 10 minutes and irradiated under blue light (λ =460-470 nm). Samples (100 μ L) are taken, diluted with DCM and directly measured via GCMS.

The reaction was purified via silica column chromatography DCM: PE 0:10 \rightarrow DCM: PE 1:9

 1 H NMR (400 MHz, CD₂Cl₂) δ 7.28 – 7.20 (m, 1H), 7.12 – 7.04 (m, 1H), 2.87 (s, 1H).

¹³C NMR (101 MHz, CD₂Cl₂) δ 140.4, 131.9, 130.3, 128.7, 37.3.

GC/MS method: Split injection, Inject. Temp. 280 °C, Oven Temp: 60 °C hold 3 min., rate 20 °C/min. to 280 °C hold 1 min. Pressure 60 kPa,

2.4 Photocatalytic hydroxylation of 4-biphenylboronic acid

4-phenylphenol



In a 2 ml flask equipped with a stir bar, 4-biphenylboronic acid (19.8 mg, 100 μ mol) *N*,*N*-diisopropylethylamine (52 μ L, 300 μ mol) and photocatalytic polymer (100 nmol photoactive unit) were dissolved in DMF (2mL). Oxygen was bubbled through the solution for 5 minutes and irradiated under blue light (λ =460-470 nm). Samples (100 μ L) were taken, diluted with DCM and directly measured via GCMS. The reaction was purified via silica column chromatography EtAc: PE 1:9 \rightarrow EtAc: PE 1:0

The reaction was purified via silica column chromatography EtAc: PE 1:9 \rightarrow EtAc: PE 1:0

 ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2)$ δ 7.58 – 7.52 (m, 1H), 7.52 – 7.46 (m, 1H), 7.45 – 7.37 (m, 1H), 7.34 – 7.24 (m, 1H), 6.94 – 6.86 (m, 1H).

¹³C NMR (101 MHz, CH₂Cl₂) δ 155.70, 141.06, 134.18, 129.12, 128.67, 127.10, 126.97, 115.98.

GC/MS method: Splitless injection, Inject. Temp. 310 °C, Oven Temp: 50 °C, rate 25 °C/min. to 310 °C hold 1 min. Pressure 43.6 kPa,

Conversion			
	C-C coupling of 4-chlorobenzyl bromide	Hydroxylation of 4-biphenylboronic acid	C-C coupling of 3-methylindol
No DIPEA	0	0	n.d
No light	0	0	0
No catalyst	0	< 5	0
Oxygen	n.d	-	0

Table S1: Blank measurements under standard conditions mentioned in the respective method without sacrificing agent, light, catalyst or under oxygen.

Photocatalyst synthesis

4-phenyl-7-(4-vinylphenyl)benzo[c][1,2,5]thiadiazole was synthesized after a previously published synthesis route.¹

¹H NMR (400 MHz, DMSO-d₆) δ 8.09 – 7.93 (m, 6H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.57 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.52 – 7.44 (m, 1H), 6.84 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.96 (d, *J* = 17.7 Hz, 1H), 5.36 (d, *J* = 11.0 Hz, 1H).

3. UV/Vis-Spectra



Figure S1: Linear fit of single photocatalytic moiety in DMF for calibration through UV/Vis-spectroscopy



Figure S2: Absorbance spectra of PMMA-BT, PAN-BT and PS-BT in DMF indicatinga change inabsorbance depending on the comonomer (left). Absorbance spectra of pure photocatalyst in toluene, DMF and ACN displaying solvatochromism

4. Tauc-Plot



Figure S3: Tauc-Plot of PMMA-BT, Pan-BT and PS-BT using a model for a direct bandgap.

5. Fluorescence Spectra



Figure S4: Fluorescence spectra of PAN-BT, PMMA-BT and PS-BT showing a blue shift in PAN-BT indicating the influence of the comonomer.



Figure S5: Excitation spectra of PAN-BT, PMMA-BT and PS-BT at 507 nm.

6. Quantum Yield



Figure S6: Quantum yield calculation of PAN-BT, PMMA-BT and PS-BT using 4,7-Diphenyl-2,1,3-benzothiadiazole at 366 nm in ACN as reference.

7. Fluorescence Lifetime





Figure S7: Fluorescence lifetime measurments of PAN-BT, PS-BT and PMMA-BT.

8. Stern-Volmer Plot



Figure S8: Stern-Volmer Plot of PAN-BT, PS-BT and PMMA-BT using DIPEA as quenching agent



Figure S9: Stern-Volmer Plot of PAN-BT, PS-BT and PMMA-BT using TPA as quenching agent

9. Dynamic light scattering



Figure S10: DLS measurments of PAN-BT, PS-BT and PMMA-BT and the calculated hydrodynamic radius.

10. FTIR-spectroscopy



Figure S11: FTIR spectra of PAN-BT, PS-BT and PMMA-BT as dry powder in KBr pellets.

<u>11. GPC</u>



Figure S12: GPC of PAN-BT, PS-BT and PMMA-BT in DMF against a PMMA standard.

12. Cyclic Voltammetry



Figure S13: CV measurments of PAN-BT, PS-BT and PMMA-BT as membranes using Nafion in ACN (NBu₄PF₆ 5.0 wt%).



PAN-BT HOMO: 1.8 V vs SCE

PAN-BT LUMO: -1.55 V vs SCE



PS-BT HOMO: 1.52 V vs SCE

PS-BT LUMO: -1.77 V vs SCE



PMMA-BT HOMO: 1.52 V vs SCE

PMMA-BT LUMO: -1.78 V vs SCE

Figure S14: HOMO (left) and LUMO (right) of PAN-BT, PS-BT and PMMA-BT. Indicating electron density shift in excited state compared to ground state

14. Cartesian coordinates

<u>PS-BT</u>

<u>PAN-BT</u>

С	-1.0272 -8.28253 -0.09701	С	-1.0272 -8.28253 -0.09701
С	0.24952 -7.7078 -0.03733	С	0.24952 -7.7078 -0.03733
С	0.3901 -6.31361 -0.01905	С	0.3901 -6.31361 -0.01905
С	-0.74616 -5.4942 -0.05786	С	-0.74616 -5.4942 -0.05786
С	-2.02289 -6.0689 -0.1158	С	-2.02289 -6.0689 -0.1158
С	-2.16349 -7.4631 -0.13386	С	-2.16349 -7.4631 -0.13386
Н	-1.13452 -9.34702 -0.11226	Н	-1.13452 -9.34702 -0.11226
Н	1 11707 -8 33344 -0 00817	Н	1 11707 -8 33344 -0.00817
н	1 36488 -5 87476 0 02734	н	1 36488 -5 87476 0 02734
н	-2 89046 -5 44324 -0 14334	н	-2 89046 -5 44324 -0 14334
н	-3 13834 -7 90194 -0 17822	н	-3 13834 -7 90194 -0 17822
C		C II	-0.50122 -3.06224 -0.04268
C C	-0.35122 - 5.50224 - 0.04508	C	-0.59122 -5.90224 -0.04308 1 72042 2 11882 0 08427
C C	-1.75045 -5.11665 -0.06427		-1.75045 -5.11665 -0.06427
C	0.79125 -3.32098 0.02133	C	0.79125 -3.32098 0.02133
C	-1.63666 -1.69086 -0.0834	C	
Н	-2./0015 -3.568/1 -0.1251	Н	-2.70015 -3.56871 -0.1251
С	0.88958 -1.82007 0.02358	С	0.88958 -1.82007 0.02358
С	-0.39749 -1.00619 -0.03177	С	-0.39749 -1.00619 -0.03177
Н	-2.5396 -1.11688 -0.11687	Н	-2.5396 -1.11688 -0.11687
С	-0.35117 0.52705 -0.04439	С	-0.35117 0.52705 -0.04439
С	0.88714 1.18716 0.0033	С	0.88714 1.18716 0.0033
С	-1.54494 1.2617 -0.09002	С	-1.54494 1.2617 -0.09002
С	0.92593 2.57582 -0.0193	С	0.92593 2.57582 -0.0193
Н	1.79615 0.62776 0.0455	Н	1.79615 0.62776 0.0455
С	-1.49743 2.64752 -0.11342	С	-1.49743 2.64752 -0.11342
Н	-2.48807 0.76104 -0.11805	Н	-2.48807 0.76104 -0.11805
С	-0.27506 3.28798 -0.08176	С	-0.27506 3.28798 -0.08176
Н	1.86302 3.098 0.02929	Н	1.86302 3.098 0.02929
S	3.16475 -2.72272 0.2883	S	3.16475 -2.72272 0.2883
Ν	1.97584 -3.93645 0.06683	Ν	1.97584 -3.93645 0.06683
N	2.14409 -1.36333 0.07466	Ν	2.14409 -1.36333 0.07466
C	-0.23323 4.81879 -0.09079	C	-0.23323 4.81879 -0.09079
н	-0.28382 5.10934 0.91605	н	-0.28382 5 10934 0 91605
C	-1 /1915 5 /3338 -0 8778	C C	-1 /1915 5 /3338 -0 8778
н		н	-1 17903 6 49308 -0 92533
н	-1 50053 5 02908 -1 84965	н	-1 50053 5 02908 -1 8/965
н С	1 05577 5 42150 0 70225	C II	1 05577 5 42150 0 70225
	1.03377 5.42139 -0.70223		
H	1.21257 5.17664 -1.7517	H	1.21257 5.17664 -1.7517
C	-2.79504 5.3181 -0.18697	C	-2.79504 5.3181 -0.18697
C	-3.96067 4.72083 -1.03347	C	-3.96067 4.72083 -1.03347
Н	-3.60909 4.52307 -1.97406	Н	-3.60909 4.52307 -1.97406
Н	-4.35224 3.84309 -0.5652	Н	-4.35224 3.84309 -0.5652
Н	-4.77589 5.50435 -1.09029	Н	-4.77589 5.50435 -1.09029
Н	-2.39962 3.22795 -0.13557	Н	-2.39962 3.22795 -0.13557
С	2.33945 5.01264 0.06724	С	2.33945 5.01264 0.06724
Н	3.04486 5.80758 -0.00063	С	-2.75568 4.74802 1.30424
Н	2.06828 4.84532 1.09512	Ν	-2.72705 4.3331 2.38956

Н	-3.08825	6.4056 -0.26347
С	-2.75708	4.76834 1.25106
С	-1.86649	5.30664 2.18033
С	-3.61311	3.73236 1.62456
С	-1.83152	4.80855 3.4826
Н	-1.19121	6.12287 1.88535
С	-3.57894	3.23467 2.92746
н	-4.31522	3.3081 0.89233
С	-2.68826	3.77247 3.85643
Н	-1.12913	5.23237 4.21494
Н	-4.25428	2.41811 3.22178
Н	-2.66055	3.37994 4.8833
С	3.04132	3.8164 -0.60207
С	3.88846	2.99746 0.14504
С	2.83006	3.55155 -1.95513
С	4.52468	1.91435 -0.46102
Н	4.05541	3.20699 1.21156
С	3.46562	2.46756 -2.56129
Н	2.16227	4.19679 -2.54407
С	4.31295	1.64906 -1.81454
Н	5.19291	1.26918 0.12765
Н	3.29854	2.25874 -3.62804
Н	4.81465	0.79497 -2.29216

Н	3.04486	5.80758	-0.00063
С	3.03826	3.82162	-0.59915
Ν	3.57434	2.96091	-1.14733
Н	2.06828	4.84532	1.09512
Н	-3.08825	6.4056	-0.26347
H H	2.06828 -3.08825	4.84532 6.4056	1.0951 -0.2634

PMMA-BT

С	-1.33724 -8.58821 -0.55482
С	-0.07169 -8.11859 -0.17826
С	0.15217 -6.74223 -0.03946
С	-0.88946 -5.8355 -0.27742
С	-2.15527 -6.30504 -0.65278
С	-2.37917 -7.68145 -0.79175
Н	-1.50798 -9.63905 -0.66135
Н	0.72373 -8.81088 0.00315
Н	1.1184 -6.38353 0.24811
Н	-2.95083 -5.61266 -0.83346
Н	-3.34556 -8.03999 -1.07883
С	-0.64296 -4.32301 -0.12681
С	-1.68649 -3.39294 -0.36303
С	0.72912 -3.79441 0.27914
С	-1.50625 -1.97813 -0.23871
Н	-2.64926 -3.76401 -0.64629
С	0.91877 -2.30694 0.40969
С	-0.26934 -1.39168 0.13059
Н	-2.34003 -1.33625 -0.43287
С	-0.12817 0.13735 0.24712
С	1.10176 0.70155 0.61162
С	-1.2294 0.96453 -0.01153

С	1.23092 2.09296 0.71622
Н	1.94235 0.06989 0.80989
С	-1.1002 2.35607 0.093
Н	-2.16871 0.5337 -0.2889
С	0.13025 2.92033 0.45608
Н	2.17005 2.52376 0.99454
S	3.01709 -3.3967 1.09807
Ν	1.83234 -4.50129 0.5397
Ν	2.15746 -1.95279 0.76336
С	0.2731 4.44956 0.56882
Н	0.04031 4.75728 1.56668
С	-0.69556 5.12915 -0.41687
С	1.71973 4.85613 0.2307
Н	1.8188 5.91877 0.30768
н	-1.94101 2.98773 -0.10449
С	2.05602 4.4118 -1.20493
Н	1.38351 4.88309 -1.89091
Н	2.39221 4.38459 0.91649
С	3.5025 4.81836 -1.54267
С	1.91398 2.88242 -1.31538
0	2.12959 2.15637 -0.31041
0	1.53715 2.28717 -2.55974
Н	4.17492 4.34694 -0.85668
Н	3.73605 4.50954 -2.54014
Н	3.60157 5.88097 -1.46584
Н	-0.46328 4.82086 -1.41487
Н	-1.70028 4.84676 -0.181
С	-0.55268 6.65861 -0.30612
С	-0.88625 7.1035 1.13008
Н	-1.89078 6.82109 1.36673
Н	-0.21256 6.63243 1.81503
Н	-0.78711 8.16619 1.2063
С	-1.52223 7.33684 -1.29167
0	-2.60676 6.77496 -1.59431
0	-1.19036 8.60495 -1.86307
С	0.8932 7.06504 -0.64624
Н	1.56663 6.5939 0.03892
Н	1.12528 6.75587 -1.64397
Н	0.99231 8.12769 -0.56996
С	0.81563 1.07808 -2.3101
Н	1.436 0.39906 -1.76322
Н	-0.06223 1.29805 -1.73916
Н	0.53324 0.63244 -3.24105
С	-2.39036 9.33396 -2.1342
Н	-2.14232 10.28296 -2.56177
Н	-2.99625 8.78067 -2.82106
Н	-2.93046 9.48363 -1.22264

15. Calibration curve



Figure S15: Calibration curve for the hydroxylation of 4-biphenylboronic acid based on isolated product and theoretical yield.



Figure S16: Calibration curve for the C-C coupling of 4-chlorobenzyl bromide based on isolated product and theoretical yield.

<u>16 GCMS</u>



Figure S17: GCMS trail of 1,2-bis(4-chlorophenyl)ethane using 1-bromo-octane as standard



Figure S18: GCMS trail of Diethyl 2-(3-methyl-1H-indol-2-yl)malonate



Figure S19: GCMS trail of 4-phenylphenol

<u>17 NMR</u>



Figure S20: ¹H NMR (400 MHz, CD₂Cl₂) of Diethyl 2-(3-methyl-1H-indol-2-yl)malonate



Figure S21: ¹³C NMR (101 MHz, CD₂Cl₂) of Diethyl 2-(3-methyl-1H-indol-2-yl)malonate



Figure S22: ¹H NMR (400 MHz, CD2Cl2) of 1,2-bis(4-chlorophenyl)ethane



145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 chemical shift [ppm]

Figure S23: ¹³C NMR (101 MHz, CD2Cl2) of 1,2-bis(4-chlorophenyl)ethane



Figure S23: ¹H NMR (400 MHz, CD₂Cl₂) of 4-phenyl phenol



Figure S24: ¹³C NMR (400 MHz, CD₂Cl₂) of 4-phenyl phenol



Figure S25: ¹H NMR (400 MHz, DMSO-d₆) of 4-phenyl-7-(4-vinylphenyl)benzo[c][1,2,5]thiadiazole



Figure S26: ¹H NMR (400 MHz, DMF-*d*₇) of PAN-BT



Figure S27: ¹H NMR (400 MHz, CD₂Cl₂) of PS-BT



1. Huber, N.; Li, R.; Ferguson, C. T. J.; Gehrig, D. W.; Ramanan, C.; Blom, P. W. M.; Landfester, K.; Zhang, K. A. I. A PMMA-based heterogeneous photocatalyst for visible light-promoted [4 + 2] cycloaddition. *Catal. Sci. Technol.* **2020**, *10*, 2092-2099.