Supporting information for

A '*Defect*ive' Conjugated Porous Poly-Azo as Multifunctional Photocatalyst

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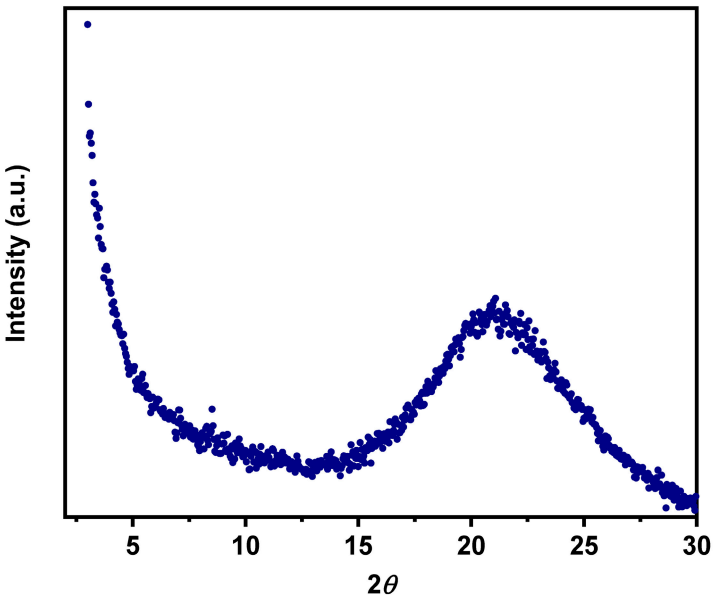

Figure S1. XRD pattern of AzoCPP showing the innate long-range structural disorder and amorphous nature.

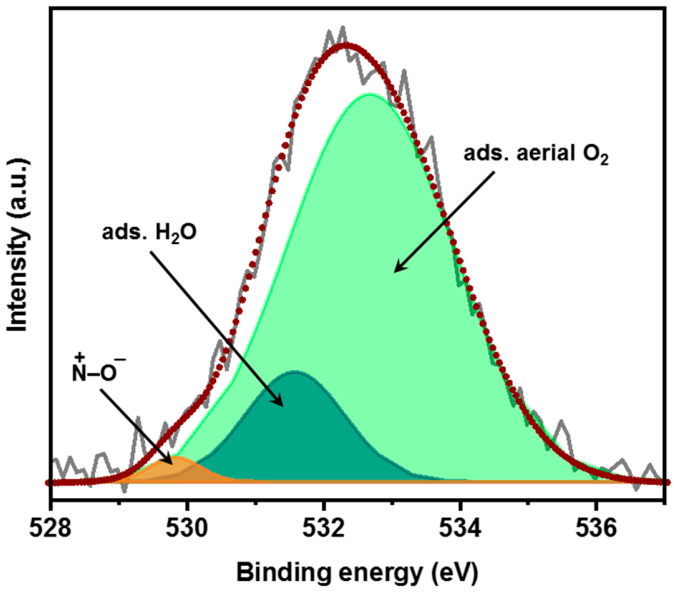

Figure S2. Deconvolution of O1s XPS pattern.

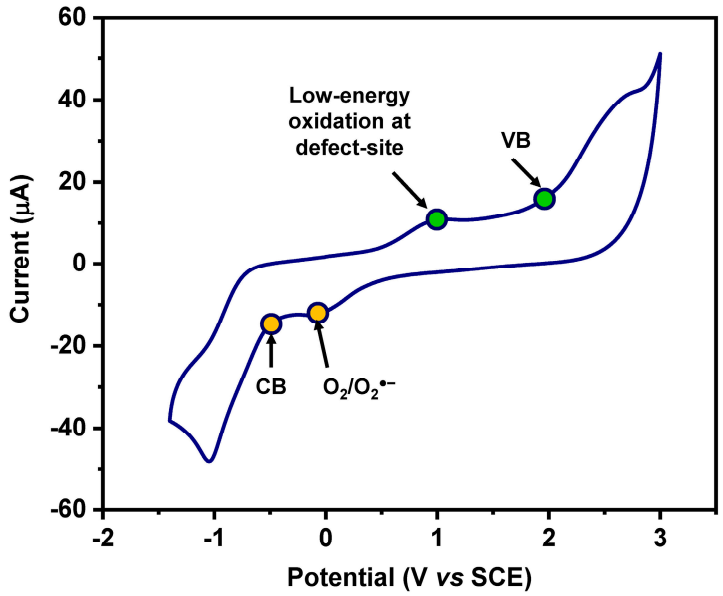

Figure S3. CV of AzoCPP. The VB and CB edge potentials were calculated from the redox onsets. Another set of oxidation and reduction peak can be perceived from the plot. The low-energy oxidation peak can be ascribed to the low oxidation potential of the inherent defect site, whereas the reduction peak was obtained due to mono-reduction of O_2 to superoxide.

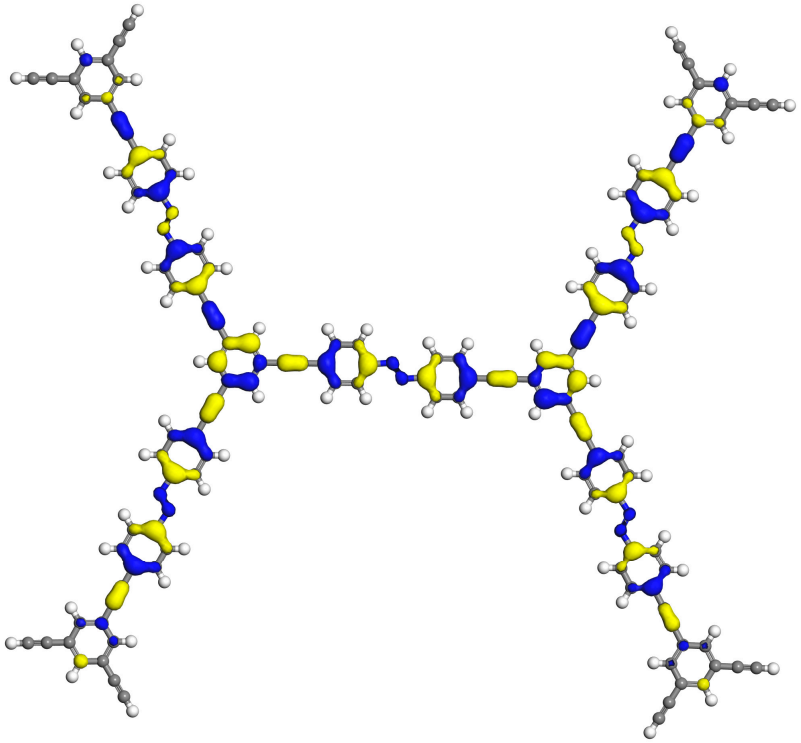

Figure S4. Theoretically obtained HOMO distribution in conjugated AzoCPP skeleton showing an extended through-plane electronic conduction.

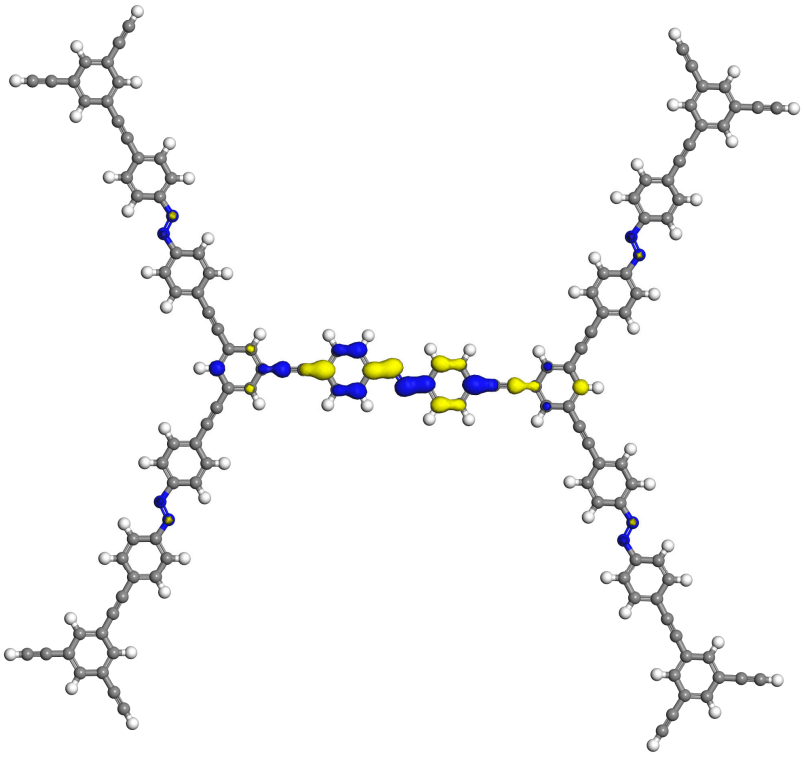

Figure S5. Theoretically obtained LUMO distribution in conjugated AzoCPP skeleton showing the excited non-bonding orbital centering on the azobenzene core.

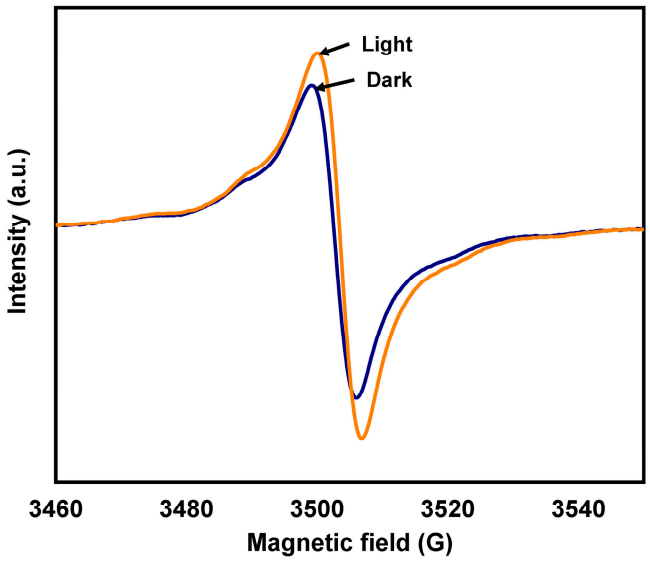

Figure S6. EPR pattern of AzoCPP in dark (blue) and under visible light illumination (orange).

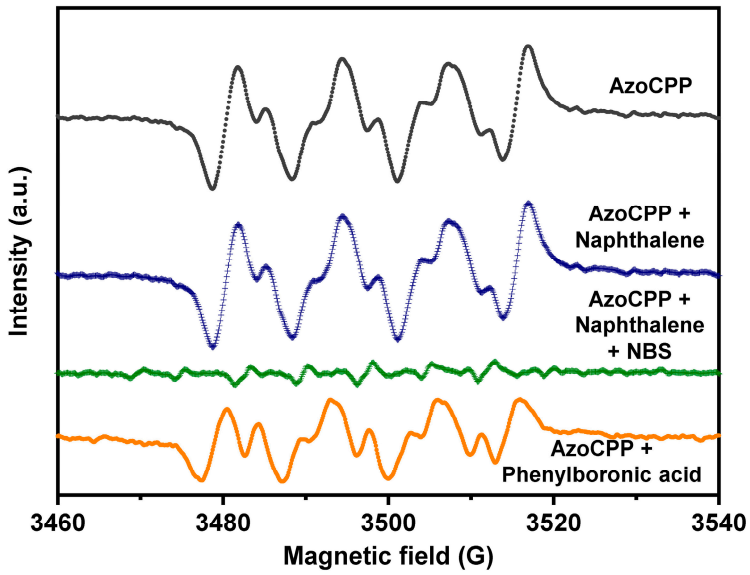

Figure S7. EPR pattern of the DMPO-superoxide adduct obtained under various situations.

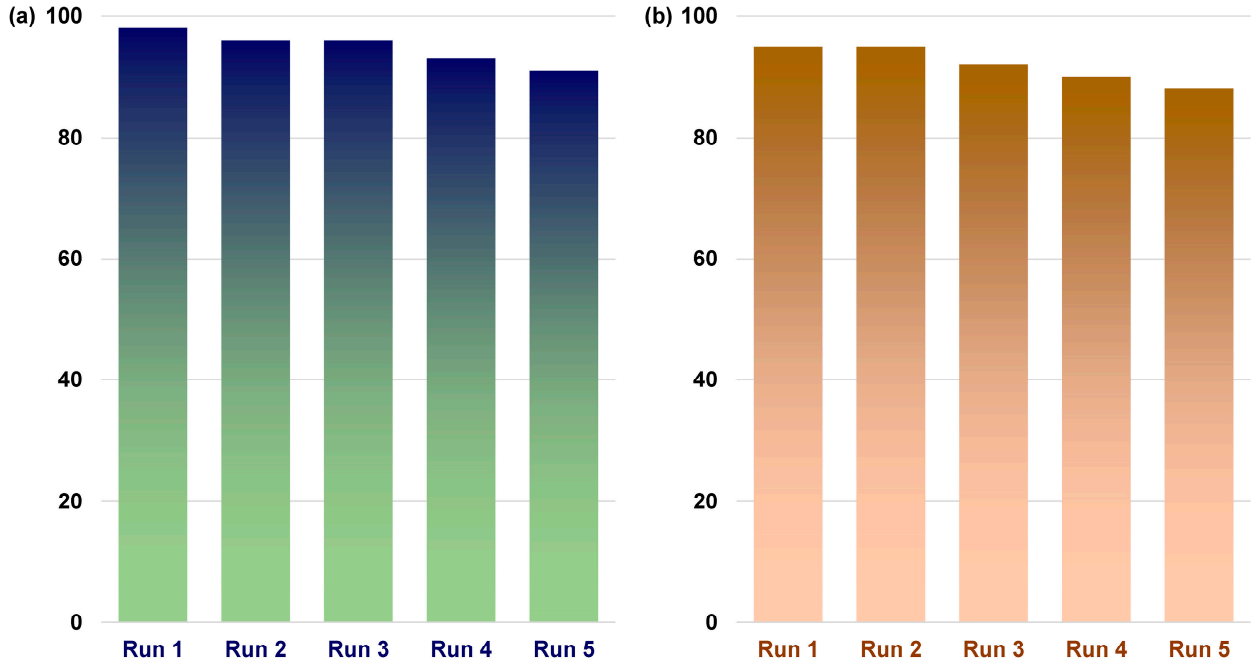

Figure S8. Recyclability test of AzoCPP for (a) oxidative bromination and (b) dehydroxylation of boronic acid. For oxidative bromination, naphthalene was used as the test substrate, whereas phenylboronic acid was chosen for dehydroxylation reaction.

Table S1. Screening conditions for photocatalytic bromination.[a]

Entry	NBS (equiv.)	Solvent	Solvent volume (mL)	Yield (%)
1	1	DMF	2	35
2	1.5	DMF	2	43
3	2	DMF	2	55
4	2	DMF/water (1:1)	2	58
5	2	Methanol	2	35
6	2	THF	2	52
7	2	Chloroform	2	21
8	2	1,2-Dichloroethane	2	18
9	2	Acetonitrile	2	82
10	2	Acetonitrile/water (1:1)	2	89
11	1.5	Acetonitrile/water (1:1)	2	87
12	1	Acetonitrile/water (1:1)	2	78
13	1	Acetonitrile/water (1:1)	3	74
14	1.5	Acetonitrile/water (1:1)	1.5	90
15	1.5	Acetonitrile/water (2:1)	1.5	94
16	2	Acetonitrile/water (2:1)	1.5	98

[a]Screening condition: Naphthalene, 0.1 mmol; AzoCPP, 5 mg; 400 nm lamp; air atmosphere.

Table S2. Control experiments for photocatalytic bromination.

Entry	Reaction condition	Yield (%)
1	Standard	98
2	Without AzoCPP	N.D.
3	In dark	12
4	In N_2 atmosphere	18

Table S3. Screening conditions for photocatalytic dehydroxylation of boronic acids.[a]

Entry	Hole scavenger (equiv.)	Solvent	Solvent volume (mL)	Yield (%)
1	Triethylamine (1)	DMF	1.5	48
5	Triethylamine (1)	Methanol	1.5	33
6	Triethylamine (1)	THF	1.5	52
7	Triethylamine (1)	Chloroform	1.5	25
8	Triethylamine (1)	1,2-Dichloroethane	1.5	34
9	Triethylamine (1)	Acetonitrile	1.5	69
	Diisopropylethylamine (1)	Acetonitrile	2	74
	Hantzsch ester (1)	Acetonitrile	2	86
10	Hantzsch ester (1.5)	Acetonitrile/water (1:1)	2	87
11	Hantzsch ester (2)	Acetonitrile/water (1:1)	2	86
12	Hantzsch ester (1.5)	Acetonitrile/water (2:1)	2	90
13	Hantzsch ester (1.5)	Acetonitrile/water (3:1)	2	92
14	Hantzsch ester (1.5)	Acetonitrile/water (4:1)	2	95

[a]Screening condition: Phenylboronic acid, 0.1 mmol; AzoCPP, 5 mg; 400 nm lamp; O_2 atmosphere.

Table S4. Control experiments for photocatalytic dehydroxylation of boronic acids to alcohols.

Entry	Reaction condition	Yield (%)
1	Standard	95
2	Without AzoCPP	N.D.
3	In dark	7
4	In N_2 atmosphere	N.D.
5	Without Hantzsch ester	trace