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Molecular Design of Donor-Acceptor-Type Organic Photocatalysts for Metal-free Aromatic C-C Bond Formations under Visible Light

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Abstract. Metal-free and photocatalytic radical-mediated aromatic C-C bond formations offer a promising alternative pathway to the conventional transition metal-catalyzed cross-coupling reactions. However, the formation of aryl radicals from common precursors such as aryl halides is highly challenging due to their extremely high reductive potential. Here, we report a structural design strategy of donor-acceptor-type organic photocatalysts for visible light-driven C-C bond formations through reductive dehalogenation of aryl halides. The reduction potential of the photocatalysts could be systematically aligned to be -2.04 V vs. SCE via a simple heteroatom engineering of the donor-acceptor moieties. The high reductive potential of the molecular photocatalyst could reduce various aryl halides into aryl radicals to form the C-C bond with heteroarenes. The designability of the molecular photocatalyst further allowed the synthesis of a high LUMO (lowest unoccupied molecular orbital) polymer photocatalyst by a self-initiated free radical polymerization without compromising its LUMO level.

Keywords: C-C bond formation; Metal-free; Photocatalysis; Organic photocatalyst; Donor-Acceptor

Direct utilization of sunlight for catalyzing chemical reactions has been considered as an inexpensive, non-polluting, and sustainable method from last few decades.[1] Since the original reports on Ruthenium bipyridyl complexes as visible light active photocatalysts[2], tremendous efforts have been made to develop the effective photocatalytic systems for organic transformation reactions. Early examples of molecular photocatalysts involve transition metal complexes[3], and further molecular organic photocatalysts[4] have been suggested as the metal-free alternatives with non-toxicity and stability. As the photocatalytic reactions mostly undergo the photogenerated-radical synthetic pathways, the molecular organic photocatalysts have strong advantage owing to designable energy structures for the activation of target molecules under light irradiation. Through a proper combination of monomeric units, the molecular organic photocatalyst can be tuned to catalyze highly challenging organic reactions, such as aromatic C-C bond formation.

Aromatic C-C bond formation via arylation reaction is a primary and key organic reaction for producing natural, pharmaceutical and high value fine chemicals.[5] Conventional way of the aromatic cross coupling is to utilize transition metal catalyst, typically palladium under the elevated temperature, giving high efficiency and selectivity[6]. However, the precious metal-based reaction has to face the issue in cost and sustainability, therefore visible light-driven C-C bond formation via radical-mediated arylation has drawn attention as a viable route of synthesizing the cross-coupled aryl products under mild condition.[7] Recent developments in photocatalytic aromatic C-C bond formation showed that the aryl precursors with relatively low reductive potentials ($E_{\mathrm{Red.}} \leq 1.0$ V vs. saturated calomel electrode (SCE)), for instance, aryl diazonium[8], diaryliodonium salts,[9] and aryl sulfonyl chlorides[10] could be reduced mainly by transition metal-based photocatalysts such as $\mathrm{Ru(bpy)_3Cl_2}$ and organic dyes such as eosin Y. In case of arylazo sulfone substrate[11], it can produce aryl radical under light irradiation even without photocatalyst owing to the photolability. In addition, the photo-induced Meerwein arylation reactions using aryl diazonium precursors have been often used to form various aromatic C-C bonds.[8b, 12] Dual catalytic systems containing a photocatalyst and a metal cocatalyt such as gold offered a useful strategy to form carbon-heteroatom bonds.[13]

Nonetheless, the formation of aryl radicals from common precursors such as aryl halides is still challenging due to their extremely high reduction potential ($E_{Red.} \geq 2.0$ V vs. SCE). Among the very few examples of suitable photocatalysts reported, König *et al.* demonstrated a perylenediimide (PDI) photocatalyst, which could reduce various aryl halides via a consecutive photo-induced electron transfer in the excited state.[14] The authors also reported a chromoselective C-C bond formation mediated by rhodamine 6G.[15] Hawker and de Alaniz *et al.* reported a 10-phenylphenothiazine (PTH) photocatalyst with a reduction potential of -2.10 V vs. SCE for photocatalytic dehalogenation reactions.[16] Effect of electron-deficient substituents on aryl substrates was also investigated by König *et al.* to lower the reduction potential of aryl halides.[17] Our group recently reported a photocatalytic Stille-type aromatic C-C bond formation catalyzed by azulene-based conjugated microporous polymer, which underwent the oxidative aryl formation mechanism.[18]

In order to thereby achieve aromatic C-C coupling reaction with aryl halide substrates under visible light, the photocatalysts should have high reductive potential, which can cleave carbon-halogen bond and generate aryl radical. The most promising way for controlling energy level of molecular organic photocatalysts is to introduce alternating composition of donor (D) and acceptor (A) moieties into the conjugated system.[19] The combination of electron-rich donor and electron-deficient acceptor leads to a compressed energy band gap by the molecular orbital hybridization and intramolecular charge transfer.[20] Thus, the intrinsic attributes of the donor and acceptor units can affect the energy level of the molecular photocatalysts, allowing a precise structural modulation for the targeted reactions.[21]

Herein, we report the structural design of donor-acceptor-type organic photocatalysts for metal-free and visible light-driven aromatic C-C bond formation via aryl radical-mediated reaction at room temperature. By a heteroatom engineering within D-A units, the reductive potential of molecular photocatalyst could be systematically elevated up to -2.04 V vs. SCE, which was able to successfully catalyze cross-coupling reaction between aryl halide and heteroarene. Thanks to the designability, the molecular organic photocatalyst was further tethered into linear chain polymer via a self-initiated free radical polymerization without compromising its reductive potential (-1.89 V vs. SCE). The unfading photoactivity in the polymeric system was showcased by the synthesis of a drug molecule through a metal-free two-step aromatic C-C bond formation.

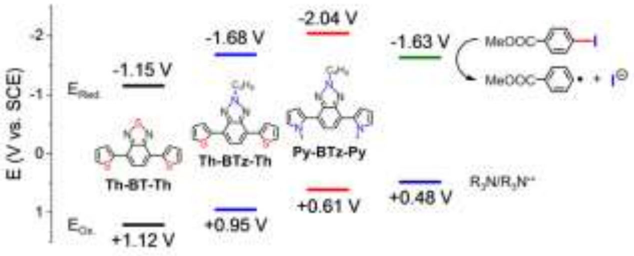


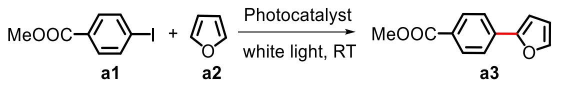
Figure 1. Structures and redox potentials of the designed molecular organic photocatalysts, oxidation potential of the sacrificial reagent R_3N (R=4-MeO-C_6H_4), and reduction potential of methyl 4-iodobenzoate substrate. E_{Red} and E_{Ox} indicate the reduction potential and oxidation potential, respectively.

To achieve extremely high LUMO band position in molecular photocatalyst, we aim to fine-tune the D-A units by substituting the type of heteroatoms. Three molecular photocatalysts were synthesized to demonstrate the structural design strategy, in particular, 4,7-di(thiophen-2-yl) benzo[c][1,2,5]thiadiazole (**Th-BT-Th**),[22] 2-butyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3] triazole (**Th-BTz-Th**), and 2-butyl-4,7-bis(1-methyl-1H-pyrrol-2-yl)-2H-benzo[d][1,2,3]triazole (**Py-BTz-Py**). Theoretical simulations of three molecular photocatalysts showed a clear difference in electron densities over D-A combinations, leading to the gradual increase in energy levels from **Th-BT-Th** to **Py-BTz-Py** (Figure S1). The structures and redox potentials of the molecular photocatalysts are shown in Figure 1. Their synthetic and characteristic details are described in the Supporting Information (SI).

The reduction potential of Th-BT-Th was measured to be -1.15 V vs. SCE via the cyclic voltammetry (CV) measurement (Figure S2). By replacing sulfur atom on the benzothiadiazole (BT) unit to nitrogen atom, the reduction potential could be elevated to -1.68 V vs. SCE, as shown in Th-BTz-Th. The lone pair of the nitrogen atom is more basic than that of sulfur, thereby makes benzotriazole ring more electron-rich, leading to higher LUMO energy level of Th-BTz-Th.[23] By further replacement of sulfur atom on adjacent thiophene units by more electron-rich 1-methylpyrrole, the reduction potential could be gradually aligned to -2.04 V, as observed by Py-BTz-Py.[24] The results correspond to the theoretical calculation and demonstrate the precise energy level control of the molecular organic photocatalysts via a heteroatom engineering on donor/acceptor moieties. Similar to the reduction potentials, tendentiously elevating oxidation potentials of the molecular photocatalysts were also observed, resulting into decreasing photo-oxidation potentials for the organic photocatalysis. The UV/vis absorption and fluorescence emission spectra of the molecular photocatalysts were displayed in Figure S3. Th-BT-Th exhibited a broader UV/Vis absorption range until ca. 550 nm with an absorption maximum at 453 nm, while Th-BTz-Th and Py-BTz-Py rather showed a narrower absorption band until ca. 450 nm, with maxima at 392 and 382 nm, respectively. The fluorescence bands of the molecular photocatalysts ranged from 420 to 800 nm with maxima at 590, 530, and 490 nm for Th-BT-Th, Th-BTz-Th, and Py-BTz-Py, respectively. Despite of the high reductive potential, Py-BTz-Py exhibited good stability, in which the fluorescent emission spectrum of Py-BTz-Py was unchanged even after the light treatment for 2 d under oxidative atmosphere (Figure S4).

Based on the aligned redox potentials of designed photocatalysts, we then conducted the photocatalytic C-C bond formation between methyl 4-iodobenzoate and furan in DMSO as a model reaction. To avoid the excess use of the electron donor and ease the purification process, we only used stoichiometric amounts of amines with respect to the aryl iodide. Tris(4-methoxyphenyl)amine ($(4\text{-MeO-}C_6H_4)_3N$) was chosen due to its low oxidation potential ($E_{\text{Ox.}}$ = 0.48 V vs. SCE), which ought to ease the electron extraction process by the excited photocatalyst. The screening and control experiments are listed in Table 1. As expected, the use of Th-BT-Th did not lead to any conversion after irradiation of white light for 24 h, which was obviously due to its insufficient reductive potential (-1.15 V vs. SCE) to reduce methyl 4-iodobenzoate ($E_{\text{Red.}}$ = -1.63 V vs. SCE) into the corresponding aryl radical (entry 1) (Figure S5). The reduction potential of Th-BTz-Th (-1.68 V vs. SCE) was slightly higher than that of the substrate, which resulted in 9% of conversion efficiency (entry 2). In contrast, conversion efficiency of 54% for the C-C bond formation was achieved using Py-BTz-Py as a photocatalyst (entry 3), resulting from its sufficient reduction potential of -2.04 V vs. SCE. The continuous light irradiation for 48 h gave a higher conversion up to 66% (entry 4). Control experiments confirmed that light, organic photocatalyst, and electron donor (amine) were mandatory for the photocatalytic C-C bond formation (entry 5-7).

Table 1. Screening and control experiments of the model reaction.



Entry[a)]	Photocatalyst	Reaction condition variations	Conversion [%][b)]
1	Th-BT-Th	-	0
2	Th-BTz-Th	-	9
3	Py-BTz-Py	-	54
4	Py-BTz-Py	Double reaction time (48 h)	66
5	Py-BTz-Py	No light	0
6	Py-BTz-Py	No photocatalyst	0
7	Py-BTz-Py	No amine	0
8	Py-BTz-Py	Et_3N as electron donor	2[c)]
9	Py-BTz-Py	Bu_3N as electron donor	9[d)]
10	Py-BTz-Py	MeCN as solvent	18[e)]
11	Py-BTz-Py	DMF as solvent	42[f)]
12	Py-BTz-Py	Light with 420 nm cut-off	23
13	Py-BTz-Py	Light with 495 nm cut-off	0

[a)] Reaction conditions: 1 equiv. (0.38 mmol) methyl 4-iodobenzoate, 20 equiv. furan, 1 equiv. $(4\text{-MeO-}C_6H_4)_3N$ as electron donor, 5 mol% photocatalyst, 2.5 ml dry DMSO as solvent, white LED (0.07 W/cm²), RT, 24 h. [b)] Conversion determined via GC-MS (Figure S6). [c)] 4% methyl benzoate as a side product. [d)] 8% methyl benzoate as a side product. [e)] no side product determined. [f)] 30% methyl benzoate as a side product.

In order to study the role of electron donor, we have also tested different alkylamines (Figure S7). By using triethylamine (Et_3N, $E_{\text{Ox.}}$ = 0.58 V vs. SCE) and tributylamine (Bu_3N, $E_{\text{Ox.}}$ = 0.43 V vs. SCE) as electron donors, only low conversions were determined (entry 8 and 9). The reason could likely lie at the high oxidation potentials of alkylamines and the formation of methyl benzoate as a side product due to abstraction of protons from alkylamines. In comparison, $(4\text{-MeO-}C_6H_4)_3N$ only acted as electron donor and not as extra proton donor during the catalytic cycle, preventing the formation of side product. The advantage of using $(4\text{-MeO-}C_6H_4)_3N$ in stoichiometric amount is that it can be fully recycled after the reaction, as shown in GC-MS spectrum (Figure S8). The solvent effect showed that the use of acetonitrile (MeCN) led to a conversion of 18% (entry 10), while DMF as a solvent gave a conversion of 42% (entry 11). Additionally, with DMF as a solvent, 30% of methyl benzoate was obtained, indicating that DMF could also act as an undesired proton donor during the reaction, as described in previous reports.[25] When the light wavelength varied, the conversion efficiency was consequently changed (entry 12 and 13). Based on the UV-vis absorption spectrum of Py-BTz-Py with the absorbance maximum at 382 nm (Figure S3), the conversion efficiency was decreased with a clear wavelength dependence, in which 23 % and 0 % of conversion were obtained with 420 nm and 495 nm cut-off of white light, respectively.

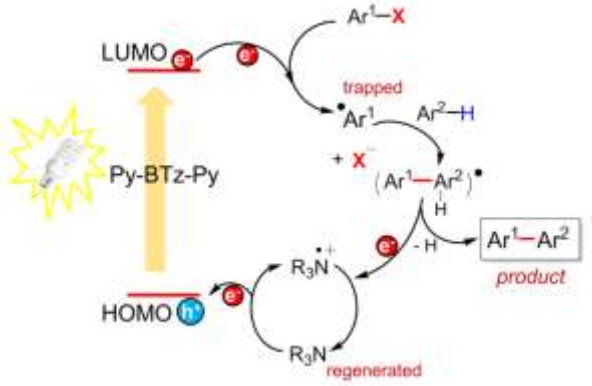


Figure 2. Proposed mechanism of the photocatalytic aryl radical-mediated C-C bond formation reaction. Ar: aryl substrates; X: halide; R_3N: sacrificial reagent as an electron donor ($R=4\text{-MeO-}C_6H_4$).

The steady-state fluorescence quenching experiments revealed that the fluorescence intensity of Py-BTz-Py could be quenched by adding either (4-MeO-C_6H_4)$_3$N or methyl 4-iodobenzoate (Figure S9). This indicates a possible electron transfer between the catalyst and both active species. To confirm the aryl radical-mediated reaction mechanism, we then conducted a reduction reaction of methyl 4-iodobenzoate using 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) as a radical trapping agent. The trapped adduct with TEMPO was determined, indicating the formation of aryl radical under visible light irradiation with Py-BTz-Py as a photocatalyst (Figure S10). The observations suggested a reaction mechanism similar to the literature, as illustrated in Figure 2.[7] The initial step was the oxidative extraction of one electron from the sacrificial reagent (R_3N) by the photogenerated hole of Py-BTz-Py, which was followed by the reductive cleavage of the carbon halogen (Ar^1-X) bond by the photogenerated electron from the LUMO level of the photocatalyst. The formed aryl radical was then added on another aryl substrate (Ar^2-H) to form the aryl-aryl radical. The aryl-aryl radical then lost one electron by the afore-obtained amine cationic radical to complete the catalytic cycle. After the deprotonation, the final product was formed.

To investigate the general feasibility of Py-BTz-Py as a photocatalyst, various aryl substrates were tested for aromatic C-C coupling reaction under the optimized reaction condition, as summarized in Figure 3. Moderate to high substituents tolerance on the aryl substrates were observed by scoping the reactions of various aryl iodides with furan. The electron-withdrawing substituents such as cyano- or trifluoro- groups (b4-b9) generally led to higher reaction yields than the electron-donating substituents (b17-b20) (Figure 3a). However, single halogen-containing substituents (b1-b3) did not give higher yields than the model substrate of methyl 4-iodobenzoate (b15). Nevertheless, aryl iodides with multiple halogen atoms gave moderate product yields (b11-b13). The reactions with the other carbonyl-containing substrates showed similar product yields to the model reaction (b14 and b16).

The scope of different arenes (Ar^2) as a coupling partner showed that the reactions with electron-rich arenes such as pyrrole could result in very high yields up to 95% (b21-b26) (Figure 3b). In particular, the formation of b25 was comparable to that from state-of-the-art example of perylenediimide-based photocatalyst (72%, 22h, at 40°C),[14] despite of using the lesser amount of counter arene and electron donor. The reaction of methyl 4-iodobenzoate with thiophene led to a slightly lower yield than the model reaction with furan (b27). The reactions with electron-deficient arenes such as phenyl (b28) and toluene (b29) showed lower product yields than the ones with electron-rich arenes. When with toluene, three different products were generated, in which o*rtho*-substituted product on toluene was mainly obtained (b29).

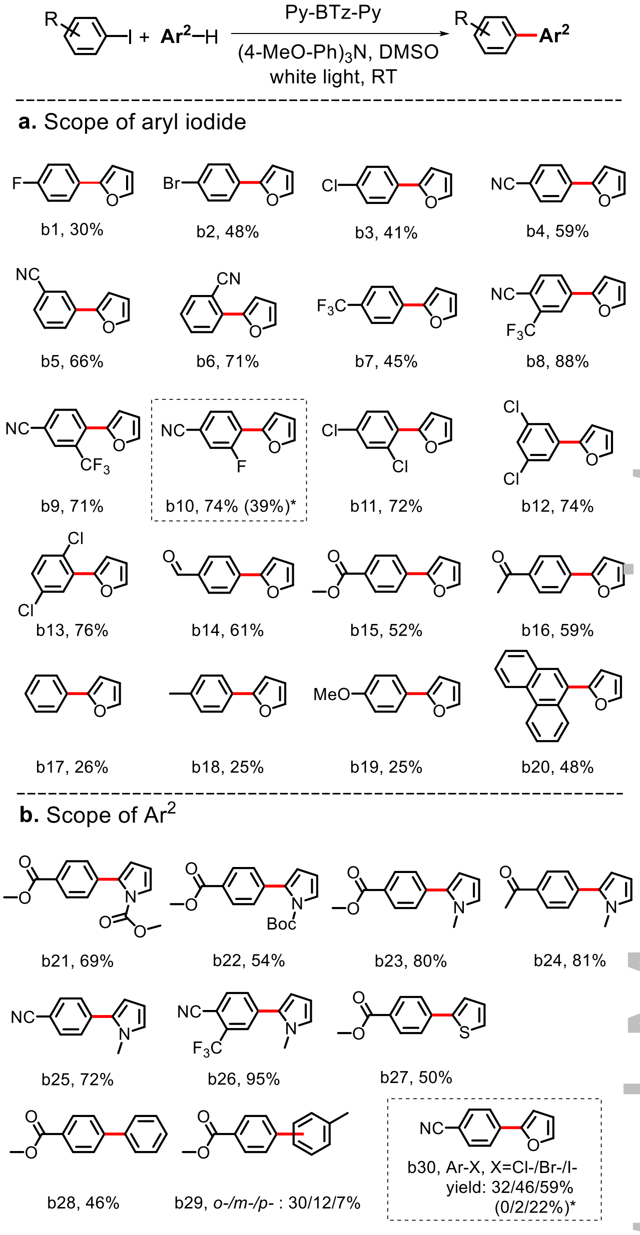


Figure 3. Scope of (a) aryl iodides with furan and (b) arenes (Ar^2) with different aryl iodides using Py-BTz-Py as a photocatalyst. Reaction conditions: 1 equiv. (0.38 mmol) aryl iodide, 20 equiv. Ar^2, 1 equiv. (4-MeO-C_6H_4)$_3$N, 5 mol% Py-BTz-Py in 2.5 ml dry DMSO, white LED (0.07 W/cm²), RT, 24 h. Isolated yields determined after chromatography. Asterisk(*) in the dotted frames indicates the product yield obtained from poly(Py-BTz-Py) as a photocatalyst.

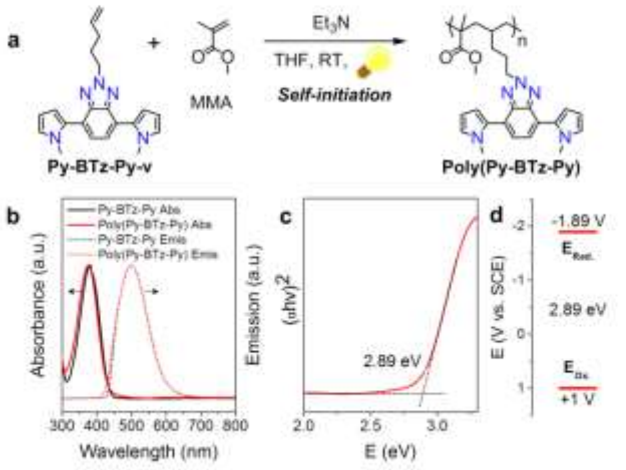


Figure 4. (a) Self-initiated free radical polymerization using Py-BTz-Py-v as a photoinitiator and a comonomer to make high LUMO polymer photocatalyst. (b) UV/vis absorption and emission spectra of Py-BTz-Py molecule and Poly(Py-BTz-Py). (c) Kubelka−Munk-transformed reflectance spectrum and (d) redox potential of Poly(Py-BTz-Py). E_{Red} and E_{Ox} indicate the reduction potential and oxidation potential, respectively.

The designable feature of molecular organic photocatalyst has been further demonstrated by the incorporation of Py-BTz-Py into polymeric structure. As shown in Figure 4a, Py-BTz-Py was simply modified to have a vinyl terminal at the end of alkyl chain on benzotriazole, giving the Py-BTz-Py-v molecule. The Py-BTz-Py-v could act as a visible light active photoinitiator as well as a comonomer for self-initiated free radical polymerization in presence of methyl methacrylate (MMA) and amine as a monomer and a cocatalyst, respectively[26]. The resulting poly(Py-BTz-Py) exhibited a molecular weight (M_n) of 21,000 g mol^{-1} with 3% of Py-BTz-Py content, proven by ^{1}H NMR spectrum (Figure S11). UV/vis absorption and emission profiles of Py-BTz-Py were retained even after the polymerization (Figure 4b). Optical band gap of poly(Py-BTz-Py) was found to be 2.89 eV from the Kubelka−Munk transformed reflectance spectrum (Figure 4c), corresponding to the cyclic voltammetry (CV) measurement (Figure 4d and Figure S12). The reduction potential of poly(Py-BTz-Py) was located at -1.89 V vs. SCE, which is sufficient for aromatic C-C bond formation reaction under visible light.

The photocatalytic activity of poly(Py-BTz-Py) was showcased by coupling reaction between halobenzonitrile and furan, since the bifuran coupled product is recently found as an effective drug molecule against methicillin-resistant *Staphylococcus aureus* infection.[27] The conversion efficiency was dependent on the reductive potentials of halobenzonitrile, in which 4-chloro-, 4-bromo-, and 4-iodobenzonitrile have the reductive potentials at -1.92, -1.80, and -1.62 V vs. SCE, respectively (Figure S5). The coupling of 4-iodobenzonitrile and furan with poly(Py-BTz-Py) showed the higher conversion yield of 22% owing to the greater overpotential, while the coupling with 4-chloro- and 4-bromobenzonitrile resulted in insignificant yields. The molecular Py-BTz-Py photocatalyst exhibited the same trend in the conversion reaction with halobenzonitriles and furan, where the increased yields were observed with respect to decreasing reductive potentials of halobenzonitriles (b30 in Figure 3). When with electron-withdrawing group of fluorine on 4-iodobenzonitrile, the product yield with poly(Py-BTz-Py) was increased up to 39% (b10 in Figure 3). Thanks to the long polymeric chain, poly(Py-BTz-Py) could be easily isolated from the reaction medium by precipitation in methanol, providing a much simpler way of purifying the products after the reaction. The regenerated poly(Py-BTz-Py) exhibited an evolution of blue-shifted peak in UV-vis emission spectrum, perhaps due to the fragmentation of photocatalytic unit from polymer after the coupling reaction (Figure S13). Such a structural change of the regenerated poly(Py-BTz-Py) led to the less conversion efficiency to produce b10, giving 26 % after 24 h of the second cycle.

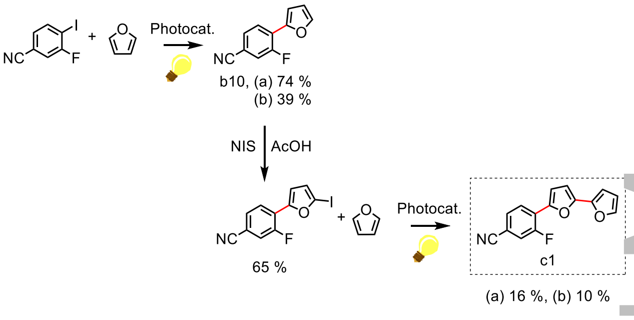


Figure 5. Metal-free synthesis of 4-([2,2'-bifuran]-5-yl)-3-fluorobenzonitrile via two-step aromatic C-C bond formation using (a) Py-BTz-Py and (b) poly(Py-BTz-Py) as photocatalysts.

The successful formation of 3-fluoro-4-(furan-2-yl)benzonitrile (b10) under visible light prompted us to conduct a stepwise coupling of furan to generate 4-([2,2'-bifuran]-5-yl)-3-fluorobenzonitrile, which is the potential drug for anticancer treatment.[27] After the iodination of b10 by N-iodosuccinimide (NIS), the additional coupling of furan was conducted in the standard reaction condition. Both Py-BTz-Py and poly(Py-BTz-Py) showed a low conversion yield to achieve the target molecule, leading to 16 and 10 % after 24 h of white light irradiation, respectively (Figure 5). Perhaps due to the electron-rich nature of furyl group on b10, the successive coupling of furan to form 4-([2,2'-bifuran]-5-yl)-3-fluorobenzonitrile (c1) resulted in the less conversion than the single step coupling reaction. Nonetheless, through the two-step aromatic C-C bond formation under visible light irradiation, the biologically-important molecule could be produced without any metal catalysts.

In summary, we have demonstrated a precise energy band position tuning of molecular organic photocatalysts for metal-free and visible light-driven aromatic C-C formation reactions. Via a facile heteroatom engineering on donor and acceptor moieties, the reduction potential of the photocatalysts could be gradually aligned to -2.04 V vs. SCE, thereby leading to a high LUMO level. Various aryl halides could be reduced to aryl radicals, which can be coupled with heteroarene substrates to form the final C-C coupled products. The designability of molecular photocatalysts further promoted the generation of linear polymer photocatalyst, showing unfading activity for synthesizing a drug molecule by two-step photocatalytic C-C coupling reaction under visible light. We believe that this study can offer a general design strategy to construct organic photocatalysts - of either molecular or macromolecular structure - with extreme high reductive potentials for tackling challenging organic transformation reactions with visible light illumination.

Experimental Section

Synthesis of Py-BTz-Py

A 100 ml Schlenk tube equipped with a stirring bar and stopper was heated under vacuum then cooled three times before 4,7-dibromo-2-(n-butyl)-2*H*-benzo[*d*][1,2,3]triazole (1 g, 3.00 mmol), 1-methyl-2-(tributylstannyl)pyrrole (2.14 ml, 6.5 mmol), and $Pd(PPh_3)_2Cl_2$ (100.8 mg, 5 mol%) were added. 15 ml dry DMF was added via syringe and the mixture was degassed under vacuum and then backfilled with nitrogen three times. It was heated under 90 °C overnight, then poured into 200 ml water and extracted with CH_2Cl_2 three times. The organic layer was washed with water twice, dried by anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified with a silica column chromatography using DCM/Hexane (1/1) as eluent, giving the final product as red brown solid (650 mg, 65%). **Th-BT-Th**, **Th-BTz-Th**, and **Py-BTz-Py-v** were produced by the similar procedure described above. The synthetic details can be found in the supporting information.

Synthesis of poly(Py-BTz-Py)

The linear polymer photocatalyst was made by the modified protocol from our previous report[28]. In a 20 ml glass vial, methyl methacrylate (0.67 ml), Py-BTz-Py-v (70 mg), and Et_3N (28 μl) were dissolved in 5 ml dry THF. The mixture was bubbled with nitrogen for 10 min and shined under white LED for 24 h under vigorous stirring. The mixture was then precipitated in methanol, filtered, and washed with methanol. The light green powder was dried under vacuum for further use, yield = 0.211 g. M_n = 21,000, M_w = 26,600, PDI = 1.27 (GPC in THF).

Standard procedure for the molecular organic photocatalyst-mediated C-C bond formation under visible light irradiation

A 25 ml Schlenk tube equipped with a stirring bar and stopper was filled with aryl halide (0.38 mmol, 1 equiv), furan (7.6 mmol, 20 equiv), tri(4-methoxylphenyl)amine (0.38 mmol, 1 equiv), organic photocatalyst (5%, 0.019 mmol) in 2.5 ml dry DMSO. When poly(Py-BTz-Py) was used as a photocatalyst, 60 mg of photocatalyst was used. The reaction mixture was degassed via three freeze-pump-thaw method and irradiated under a white light (power: 0.07 W cm^{-2}, $\lambda > 420$ nm) under argon atmosphere. The final conversion was determined by GC-MS after 24 h irradiation. To obtain the pure product, the mixture was poured into 20 ml water and extracted by CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$, and the solvent removed under vacuum. The crude product was then purified over a silica column chromatography to afford the desired product using petroleum ether/ethyl acetate (95:5 or 90:10) as eluent.

Acknowledgements

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