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## Asymmetric Covalent Triazine Framework for Enhanced Visible Light Photoredox Catalysis via Energy Transfer Cascade

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**Abstract:** The construction of complex multiple component semiconductor photocatalyts allows enhanced catalytic efficiency via multiple charge and energy transfer, which mimics the nature photosystems. However, the efficiency of single component semiconductor photocatalysts is usually inhibited due to the fast recombination of the photo-generated excitons. Here, we report the design of an asymmetric covalent triazine framework as efficient single component organic semiconductor photocatalyst. Four different molecular donor-acceptor domains are obtained within the network, leading to an enhanced photogenerated charge separation via intramolecular energy transfer cascade. The superior photocatalytic efficiency of the asymmetric covalent triazine framework over its symmetric counterparts was demonstrated via the visible light-driven formation of benzophosphole oxides from diphenylphosphine oxide and diphenylacetylene.

Direct use of solar energy to drive photoredox reactions is an environmentally friendly, non-toxic and highly sustainable alternative to the traditional thermal reaction conditions.<sup>[1]</sup> In nature photosynthesis, a series of stepwise energy and charge transfer processes is involved to enhance the photogenerated charge separation and transfer process.<sup>[2]</sup> Taking the nature photosystem as a role model, chemists and materials scientists have designed a wide variety of multiple component photocatalytic systems in order to increase their photocatalytic efficiency. For example, the construction of heterojunction metal semiconductors<sup>[3]</sup> and bridged transition metal complexes<sup>[4]</sup> have been reported to greatly promote the photogenerated charge separation and transfer. Recently, the state of art metal-free photocatalyst, carbon nitrides<sup>[5]</sup> with different metal loadings,<sup>[6]</sup> or doping with heteroatoms,<sup>[7]</sup> conjugated organic dyes,<sup>[8]</sup> or other metal semiconductors<sup>[9]</sup> have been reported as efficient strategy to overcome the fast recombination of the photogenerated excitons during the catalytic process.

Macromolecular organic semiconductor photocatalysts have demonstrated their distinct advantage in the ease of tuning the optoelectronic properties by appropriate choice of donor and acceptor units as well as their alignment ordering.<sup>[10]</sup> They have been employed as a stable and efficient platform for visible light photoredox reactions as water splitting,<sup>[11]</sup> selective oxidation of organic compound,<sup>[12]</sup> and C-C bond formation reaction<sup>[13]</sup> etc. To reach higher photocatalytic efficiency, the enhanced charge

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separation and thermodynamically favorable band positions are of great importance.<sup>[14]</sup> Indeed, several synthetic strategies have been recently applied to improve the photocatalytic efficiency of the organic semiconductors, including copolymerization, molecular geometry design<sup>[15]</sup> and heterojunction formation<sup>[16]</sup>. However, the photocatalytic efficiency of the single component organic semiconductor photocatalysts is usually limited due to the fast recombination of the photo-generated excitons.<sup>[17]</sup> New design strategies are highly needed.



**Figure 1.** (a) Representative repeating unit structure of the asymmetric network asy-CTF containing 4 different molecular D-A domains (M1-M4), (b) its symmetric counterparts CTF-Th and CTF-Th-Ph containing only a single D-A domain, and (c) HOMO and LUMO levels of the 4 different D-A domains within asy-CTF calculated at the B3LYP/6-31G (d) level.

Herein, we report the design of an asymmetric covalent triazine framework (CTF) as single component organic semiconductor photocatalyst possessing photogenerated energy transfer cascade. Four different molecular donor-acceptor domains were obtained within the backbone, leading to an photogenerated broad enhanced absorption range. intramolecular energy transfer and sufficient photoredox potential. Here, the alternating and symmetric donor-acceptor structure, which is characteristic for single organic semiconductor photocatalysts, is non-existent within the asymmetric network. Compared to the symmetric CTFs containing similar donor and acceptor moieties, the superior photocatalytic efficiency of the asymmetric CTF was demonstrated via the visible light-driven

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formation reaction of benzophosphole oxides from diphenylphosphine oxide and diphenylacetylene as the model photoredox reaction.

The asymmetric CTF (asy-CTF) was synthesized via trifluoromethanesulfonic acid (TfOH) catalyzed trimerization<sup>[18]</sup> of 5-(4-cyanophenyl)thiophene-2-carbonitrile in its solid state (Figure 1a). For comparison, two symmetric CTFs containing thiophene and phenylthiophene with triazine core were prepared as reference materials, referring to CTF-Th and CTF-Th-Ph, respectively (Figure 1b). The synthetic details and characterization data are described in the Supporting Information (SI). The structure of asy-CTF suggested the formation of four different combinations containing triazine unit as electron acceptor and thiophene or phenyl units as electron donor. The observation was confirmed by the control reaction of a 1:1 mixture of benzonitrile and thiophene-2-carbonitrile, which led to the formation of the 4 model D-A combinations (M1-M4) (Figure S1). Theoretical simulations of the 4 different D-A combinations calculated at the B3LYP/6-31G\* level showed different electron densities on the HOMO and LUMO levels (Figure 1c and Figure S2).



Figure 2. (a) Solid state <sup>13</sup>C CP NMR spectra, (b) UV/Vis DR spectra, (c) HOMO and LUMO levels, (d) time-resolved photoluminescence spectra, and (e) photocurrent of all three CTFs.

Transmission electron microscopy (TEM) images of CTFs showed a similar fused particle-like morphology (Figure S3). Fourier transform infrared (FT-IR) spectra of the CTFs showed the characteristic bands around 1438, 1348 and 800 cm<sup>-1</sup>, which

can be assigned to the aromatic C-N stretching and breathing modes in the triazine unit (Figure S4).<sup>[19]</sup> Solid state <sup>13</sup>C crosspolarization magic-angle-spinning (CP-MAS) NMR spectra of the symmetric CTFs showed a single sharp peak at 167.3 ppm for CTF-Th and 170.4 ppm for CTF-Th-Ph, which can be assigned to the sp<sup>2</sup> carbon in the triazine unit (Figure 2a). In contrast, asy-CTF exhibited a relatively broad signal from 180 to 160 ppm, which is assigned to the fusion of the sp<sup>2</sup> carbons in the triazine units connected both to the thiophene and phenyl units. This result clearly indicated the formation of the different D-A combinations within the asy-CTF backbone. The exact elemental compositions of CTFs were further confirmed by X-ray photoelectron spectroscopy (XPS) as displayed in Figure S5. Brunauer-Emmett-Teller (BET) surface areas were determined to be 78 m<sup>2</sup>/g for CTF-Th, 62 m<sup>2</sup>/g for CTF-Th-Ph, and 52 m<sup>2</sup>/g for asy-CTF (Figure S6). The pore sizes of three CTFs were distributed in the mesoporous range. Additionally, powder X-ray diffraction (PXRD) patterns indicated the amorphous character of the CTF samples (Figure S7). It is worth to note that the all three CTF materials exhibit excellent thermal stabilities up to ca. 500 °C under oxygen atmosphere (Figure S8).

UV/Vis diffuse reflection spectra (DRS) of the three CTFs showed a broad absorption range up to 800 nm (Figure 2b). Optical band gaps of 2.48 eV for CTF-Th, 2.42 eV for CTF-Th-Ph and 2.30 eV for asy-CTF could be derived from the Kubelka-Munk-transformed reflectance spectra (Figure S10).<sup>[20]</sup> Cyclic voltammetry (CV) measurement further revealed the lowest unoccupied molecular orbital (LUMO) of asy-CTF at -1.30 V vs SCE, which is higher than that of CTF-Th-Ph at -1.24 V and that of CTF-Th at -1.02 V vs. SCE (Figure S11). The corresponding HOMO levels could be observed to be +1.0 V, +1.18 V and +1.46 V for asy-CTF, CTF-Th-Ph and CTF-Th, respectively (Figure 2c).

Time-resolved photoluminescence (TRPL) spectroscopy at the excitation wavelength at 400 nm revealed a fluorescence lifetime of 1.27 ns for asy-CTF, which was shorter than that of CTF-Th and CTF-Th-Ph with 1.66 ns and 1.57 ns, respectively (Figure 2d). The slightly shorter fluorescence lifetime of asy-CTF compared to CTF-Th and CTF-Ph-Th might indicate an improved delocalization and thereby more non-radiative recombination of the excitons within asy-CTF, which led to a reduction of the lifetime. To get a deeper insight, we then recorded the TRPL spectra of asy-CTF and CTF-Th for a select time traces between 0.5-7.5 ns as a direct comparison (Figure S12a). Asy-CTF exhibited a broader and higher energy emission peak than steady-state PL as shown in Figure S9. The resulting decayassociated spectra (DAS) via global analysis scheme<sup>[21]</sup> (Figure S12b) showed a longer lifetime of asy-CTF at longer emission wavelength (see detailed note for Figure S12), suggesting rather a possible excitation energy transfer than charge transfer within asy-CTF. To reveal the multiple successive energy transfer steps from higher to lower energy moieties along a broad spectral range for asy-CTF, we conducted fluorescence quenching experiments with the model molecules M1 and M4 in steady states. The quenched fluorescence of M1 by M4 confirmed the energy transfer mechanism inside asy-CTF (Figure S13). The photocurrent measurements (Figure 2e) showed that asy-CTF exhibited an enhanced photocurrent compared to its symmetric counterparts, which revealed the improved light-induced charge mobility within asy-CTF.

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Benzophosphole oxide derivatives have recently attracted much attention in the field of material chemistry due to their unique photophysical and electronic properties.<sup>[22]</sup> Common synthetic approaches to generate benzophosphole oxides usually involve the utilization of transition metal catalysts and elevated temperature.<sup>[23]</sup> Very few reports on the photocatalytic method have been reported. Here, to investigate the photocatalytic activities of the CTF materials and confirm the superior catalytic performance of asy-CTF for organic photoredox reactions, the visible light-promoted formation of 1,2,3-triphenylphosphindole 1oxide (3a) from diphenylphosphine oxide (1a) and diphenylacetylene (2a) was chosen as a model reaction in the presence of a base and *N*-ethoxy-2-methylpyridinium tetrafluoroborate as an oxidant.<sup>[24]</sup> As shown in Figure 3a, the reaction catalyzed by asy-CTF reached a conversion of 93% after 24 hours, which was significantly higher than those catalyzed by the symmetric conjugated polymers CTF-Th (22%) and CTF-Th-Ph (63%). In the absence of the photocatalyst, light or oxidant, no product was obtained (Table S1, entries 4-6), indicating the indispensable role of the three components. Additionally, the effect of the solvents and bases were also studied. DMF and NaHCO<sub>3</sub> appeared to be the most suitable reagents to achieve the high reaction conversion (Table S1, entries 7-12). Asy-CTF exhibited the higher catalytic efficiency than CTF-Th and CTF-Ph-Th under single wavelengths (420 nm and 495 nm), implying the synergetic effect of broader light absorption and enhanced energy transfer cascade within the asymmetric network (Figure S14). Repeating experiment of the model reaction demonstrated that asy-CTF could be reused up to five cycles without losing its catalytic efficiency (Figure S15) and physicochemical properties (Figure S16).



**Figure 3.** (a) Reaction dynamics in photosynthesis of 1,2,3triphenylphosphindole 1-oxide catalyzed by asy-CTF, CTF-Th-Ph and CTF-Th; b) Stern-Volmer quenching measurements with CTFs and oxidant (I<sub>0</sub> and I are the integrated emission intensities of photocatalysts in DMF in the absence and presence of the oxidant, respectively).

To better understand the photo-induced electron transfer between the CTFs and substrates, and explain the superior photocatalytic activity of asy-CTF, we further conducted fluorescence quenching experiments (Figure S17, S18). The fluorescence intensity of CTFs was gradually attenuated by adding the oxidant, while the addition of DPPO did not significantly affect the fluorescence intensity. Meanwhile, the formed ethoxyl radical intermediate was also detected by electron paramagnetic resonance (EPR) experiments with a-phenyl-Ntert-butylnitrone (PBN) as a radical trapping agent (Figure S19a).<sup>[25]</sup> Remarkably, the phosphinoyl radial could be identified along with the disappearance of the ethoxyl radical signals followed by the addition of diphenylphosphine oxide into the mixture (Figure S19b).<sup>[26]</sup> These results clearly demonstrated that the electron transfer from the photocatalyst to the oxidant ought to be the initial step of the photocatalytic cycle. Moreover, the slope of the Stern-Volmer curve of the oxidant to quench asy-CTF was determined to be 127.4, which was 2.6 and 6.3 times higher than those of CTF-Th-Ph (49.7) and CTF-Th (20.3). This indicates a considerably more efficient electron transfer between asy-CTF and the oxidant in comparison to the cases of the symmetric polymer networks. The reason is most likely the highest overpotential ( $\Delta E$ = 0.52 V) between the LUMO of asy-CTF (-1.30 V vs SCE) and the reduction potential of the oxidant (-0.78 V vs. SCE) (Figure S20), combined with the superior photo-induced electron conductivity as demonstrated by the photocurrent measurement.

On the basis of the above observations, we proposed a plausible mechanism similar to the literature,<sup>[24]</sup> as displayed in Figure S21. Under visible light irradiation, the reaction is first initiated by a single electron transfer (SET) event from the LUMO N-ethoxy-2-methylpyridinium of the photocatalyst to tetrafluoroborate to form the ethoxyl radical. The ethoxyl radical subsequently undergoes via hydrogen abstraction from the secondary phosphine oxide to obtain the phosphinoyl radical. The phosphinoyl radical then adds to the alkyne to form the alkenyl radical. Then intermolecular cyclization between the alkenyl radical and the phenyl ring of the phosphine oxide leads to the cyclohexadienyl radical, which can be readily oxidized by the photogenerated holes of the photocatalyst to generate a cation intermediate. Finally, after deprotonation in the presence of base, the desired final product is obtained.

To investigate the general feasibility of asy-CTF as an efficient photocatalyst, we then extended the scope of the substrates. As summarized in Figure 4, the symmetric diaryl-substituted alkynes with both electron-rich and electron-withdrawing groups can react smoothly with DPPO to afford the corresponding products in excellent yields (3b-f). The symmetric alkyl alkyne 4-octyne can also be employed in current reaction with moderate yield (3g). Remarkably, all the asymmetric phenylacetylenes tested here could react with DPPO in a regioselective manner to form the 2substituted 1,3-diphenyl-1H-phosphindol-1-ones with moderate yields (3h-k). The high regioselectivity can be attributed to the stabilizing effect for the formed alkenyl radical by the adjacent of the phenyl rings.<sup>[27]</sup> Furthermore, the scope of phenylphosphine oxides with various substituted groups was also examined. The monophenylphosphine oxides bearing alkyl groups could be coupled with diphenylacetylene to afford the corresponding products with moderate to good yields (3I-o). For the diphenylphosophine oxide derivatives bearing electron-rich or electron-poor groups at the aromatic rings, regioisomers were obtained (3p-f), which was probably caused by the new C-P bond formation via aryl migration.[23a, 28]

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Figure 4. Scope of substrates for photocatalytic synthesis of benzophosphole oxides using asy-CTF as a photocatalyst.

In summary, a simple structural design of asymmetric covalent triazine framework as an efficient visible light-active photocatalyst for photoredox reactions has been introduced. By incorporating the asymmetric building block, four different molecular donor-acceptor domains were obtained within the backbone structure. The asymmetric donor-acceptor structure led to enhanced photogenerated charge separation, intramolecular electron transfer and sufficient photoredox potential. The asymmetric CTF demonstrated its superior photocatalytic efficiency compared to the symmetric CTFs containing similar donor and acceptor moieties, proven by the photocatalytic reaction of benzophosphole formation oxides from diphenylphosphine oxide and diphenylacetylene derivatives. We believe that this study could establish a simple but new design strategy of organic semiconductor photocatalysts for a broader range of applications such as water splitting and CO2 reduction etc.

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**Keywords:** Asymmetric organic semiconductor • Photocatalysis • Covalent triazine framework • Donor acceptor • Metal-free

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