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A Triazine Functionalized Porous Covalent Organic Framework for Photo-organocatalytic *E-Z* Isomerization of Olefins

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Supporting Information Placeholder

ABSTRACT: Visible light-mediated photocatalytic organic transformation has drawn significant attention as an alternative process for replacing thermal reactions. Although precious metal/organic dyes based homogeneous photocatalysts have been developed, their toxic and non-reusable nature makes them inappropriate for large-scale production. Therefore, we have synthesized a triazine and a keto functionalized non-metal based covalent organic framework (TpTt) for heterogeneous photocatalysis. As the catalyst shows significant absorption of visible light, it has been applied for the photocatalytic uphill conversion of *trans*-stilbene to *cis*-stilbene in the presence of blue LEDs with broad substrates scope *via* an energy transfer process.

Alkene/olefin functional groups are essential organic building units in many synthetic polymers and drugs.^{1a-c} Stereoselective synthesis of olefins is important due to their large scope of applications in synthesizing anticancer drugs,^{1d,e} scintillators,² chromatic lasers³ and industrial dyes.^{4,5} However, most of the methods to synthesize alkenes lead to the formation of the thermodynamically more stable *trans* (*E*) form while the direct synthesis of the energetically less stable *cis* (*Z*) form is remarkably challenging and has been restricted to a limited number of available synthetic methods.⁶ Most of these synthetic methods lack high stereoselectivity and often require high energy and expensive homogeneous metal catalysts.⁷ The probable solution for an economic and stereoselective synthesis of the *Z* isomer should be to follow the conventional photo-assisted *E* to *Z* isomerization strategy. However, most of the common olefin compounds lack absorption in the visible range. Thus, the *E* to *Z* transformation can happen only by a high energy UV radiation approach, which is neither a green, nor a safe process.⁸ The alternative solution for this problem would be to use more abundant visible light to perform this *E* to *Z* isomerization of olefins with the help of a photocatalyst. However, designing such catalyst is a challenging task as the ideal photocatalyst needs to feature high photochemical stability, optimum band gap, absorption maxima in the visible range, and a long-lived excited state.⁹ In the literature, photocatalysts such as metal polypyridyl complexes,¹⁰ organic dyes such as riboflavin,¹¹ and aromatic keto

compounds¹² have been used for the *E* to *Z* isomerization of alkenes. However, the recyclability of these expensive photocatalysts becomes a key issue due to their homogenous nature and low photochemical stability. Hence, there is a high demand for developing a novel heterogeneous, chemically stable photocatalyst for the economic and energy efficient *E* to *Z* conversion of alkenes.

Covalent Organic Frameworks (COFs), a novel class of porous crystalline polymers, have recently emerged as heterogeneous catalysts for various organic transformations.¹³ COFs, because of their highly ordered, predesignable and functionalizable porous structures, allow precise integration of catalytic centers in the framework matrix in a well-defined manner. Keeping all these features in perspective, we have successfully synthesized a novel heterogeneous COF based porous photocatalyst for the *E* to *Z* isomerization of alkenes. The photocatalytic COF is constructed from two distinct photoactive building blocks (triazine and β -ketoenamine) having unique photo-sensitizing properties. The triazine core should catalyze *E* to *Z* photo-isomerization of an alkene by facilitating strong π - π interaction with the *E* alkenes.¹⁴ Additionally, keto functionalities present in the β -ketoenamine core could help to enhance the lifetime of the excited triplet state.^{12,15} Moreover, due to the irreversible nature of the β -ketoenamine formation reaction, the novel triazine functionalized hybrid COF can offer high chemical stability even upon irradiation of light.^{13f,g}

The COF (TpTt) was constructed by performing reaction between melamine/1,3,5-Triazine-2,4,6-triamine (Tt) and 2,4,6-Triformylphloroglucinol (Tp) aldehyde (Figure 1a, Section S2). Previously, several polymers with triazine moiety were made in the presence of a metal catalyst and higher temperatures.¹⁶ Therefore, finding a suitable method for synthesizing a crystalline porous TpTt COF from a melamine building block without using a metal catalyst was very challenging due to its poor reactivity. After several trials with different solvent combinations, we have produced a moderately crystalline TpTt COF using the DMAc:DMSO (2:1) solvent combination. The PXRD patterns of TpTt display two main characteristic peaks at $2\theta = 9.7^\circ$ and 27.4° , which correspond to the reflections from the 100 and 002 planes respectively (Figure 1b). From the *d* spacing of the 002 peaks, we have calculated the interlayer π - π stacking distance between the individual COF layers to be 3.5 Å (Figure 1c). To find out a

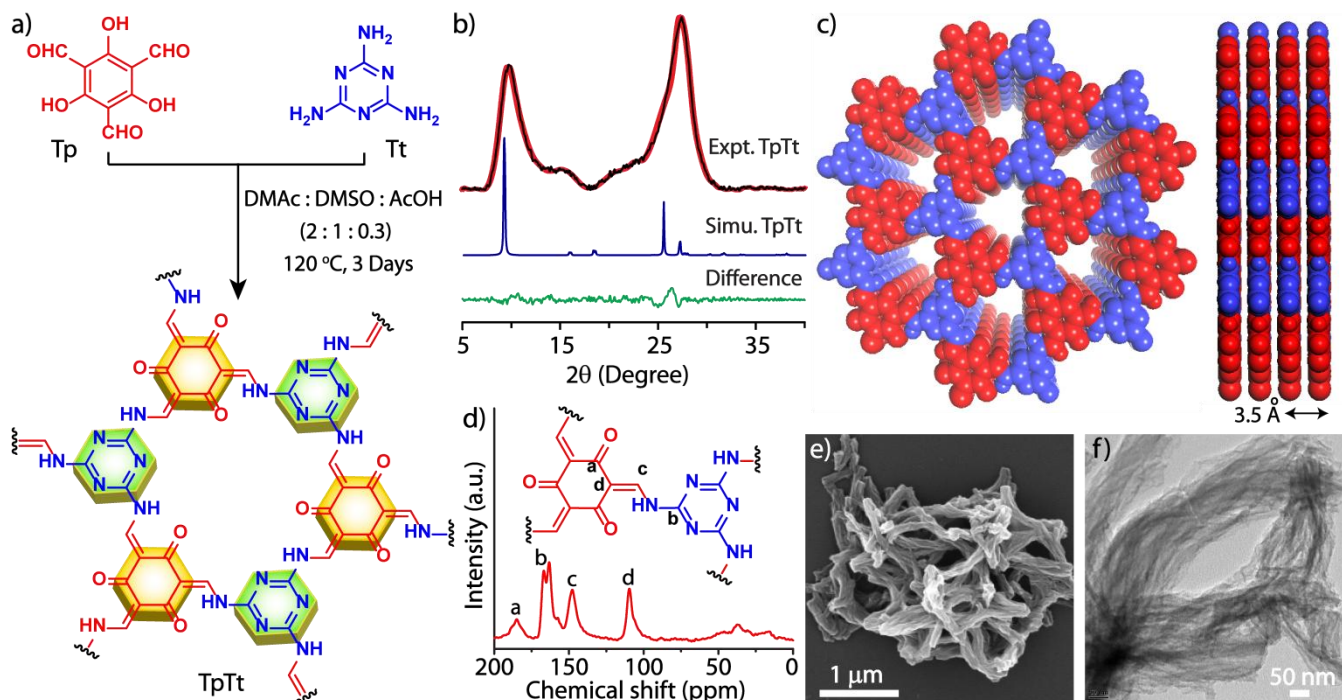


Figure 1. (a) Schematic representation of the TpTt synthesis. (b) Comparison of the experimental PXRD patterns of TpTt (black) with the simulated (blue) simulated after Pawley refinement (red), and difference plot (green). (c) Space-filling AA eclipsed stacking models of the TpTt along c and a-axis direction. (d) ^{13}C CP-MAS solid-state NMR and (e) SEM and (f) TEM images of TpTt.

reasonably fitting modeled structure of TpTt, several stacking possibilities such as AA eclipsed, AB staggered and AA inclined models were constructed. From the Pawley refinement studies, we have observed that the simulated PXRD patterns of the AA eclipsed and AA inclined structures have a decent agreement with the experimental PXRD pattern (Section S3, Table S1). The successful incorporation of β -ketoenamine links in TpTt is indicated by the appearance of intense peaks at 1620 cm^{-1} ($-\text{C}=\text{O}$), 1523 cm^{-1} ($-\text{C}=\text{C}$) and 1236 cm^{-1} ($-\text{C}-\text{N}$) in the FTIR spectra (Figure S3). The ^{13}C CP-MAS spectra of TpTt displays characteristic signals of the carbonyl carbon ($-\text{C}=\text{O}$) of the β -ketoenamine core at 184.9 ppm and the doublet peaks at 166.8 ppm and 163.2 ppm for aromatic carbons of the triazine core.¹⁷ The rest of the peaks corresponding to the sp^2 carbons appear in the range of 147.7 ppm to 109.5 ppm (Figure 1d, S4). SEM (Figure 1e, S9) and TEM (Figure 1f, S10) images reveal that TpTt crystallites possess fibrillar morphology. Thermogravimetric analysis (TGA) under N_2 atmosphere shows the thermal stability of TpTt up to $200\text{ }^\circ\text{C}$ (Figure S7).

The N_2 adsorption isotherm of TpTt COF displays a type-I reversible isotherm with $277\text{ m}^2\text{g}^{-1}$ accessible surface area calculated by using the Brunauer–Emmett–Teller (BET) method. Furthermore, nonlocal density functional theory (NLDFT) calculations reveal that TpTt shows a narrow pore size distribution, with a peak maxima at 1.3 nm (Section S6, S7). The pore size distribution of TpTt and the length of the *trans*-stilbene indicate that the maximum reaction happens on the surface of the crystallites. It is experimentally observed that the porosity and the crystallinity in the framework structure (TpTt) play an important role during the photo-organocatalytic *E-Z* isomerization process and exhibit better catalytic performance compared to similar amorphous polymer (TpTt-Poly) (Section S19). The solid-state UV-Vis diffuse reflectance spectrum of the TpTt powder shows broad absorption spectra in the visible region, having a two peak maximum at 350 nm and 525 nm .

In comparison to the starting materials Tp (254 and 340 nm) and Tt (250 nm), the absorption maxima of TpTt appears at a higher wavelength in the visible range due to extended conjugation (Figure 2a). The optical band gap of TpTt is calculated as 2.74 eV from the UV-Vis spectra by using the Tauc plot (Figure S8). Also, we have calculated (using DFTB) the energy difference between the HOMO and LUMO orbitals of TpTt COF in several stacking modes. Among them, the theoretical energy difference between the HOMO and LUMO of TpTt in the AA slip mode is in good agreement with the calculated energy difference from experiment (Figure 3b, S17, Table S6, S7). The visible light absorption capacity, together with the ideal band gap, makes TpTt an ideal catalyst for the *E* to *Z* photo-isomerization reaction.

After observing the significant visible light absorbing ability of the photocatalyst, the activated TpTt catalyst is directly utilized for the *trans* to *cis* isomerization reaction by choosing *trans*-stilbene as the benchmark substrate for the optimization process. When the *trans*-stilbene (0.5 mmol) in 5 mL DMF solvent in the presence of a catalytic amount of TpTt COF (4 mg) was irradiated using blue LEDs at room temperature, we have observed the formation of *cis*-stilbene (GC analysis). A 20% yield of *cis*-stilbene is observed after the initial 2 hours of reaction time. The yield of the *cis*-stilbene increased steadily with reaction time and obtained the maximum yield (90%) at an exposure time of 18 hours (Figure 2b). Later, we have screened the effect of various solvents and observed that DMF is the optimal solvent for this transformation. It gave 90% yield of the *cis*-stilbene under standard reaction condition (Table 1, entry 1, Table S2). As the amount of catalyst and solvent increase, the formation of the product also increases and 4 mg TpTt catalyst and 5 mL DMF solvent are optimal for this transformation (Table S3, S4). Under similar photocatalytic conditions, melamine (Tt) yielded *cis*-stilbene with a trace amount (Table 1, entry 3). To understand the necessity of the COF catalyst in this isomerization reaction, we have conducted a blank photocatalytic experiment without using TpTt in the presence of visible light (Table 1, entry 2). No peak is observed in the GC corresponding to *cis*-stilbene, which signifies

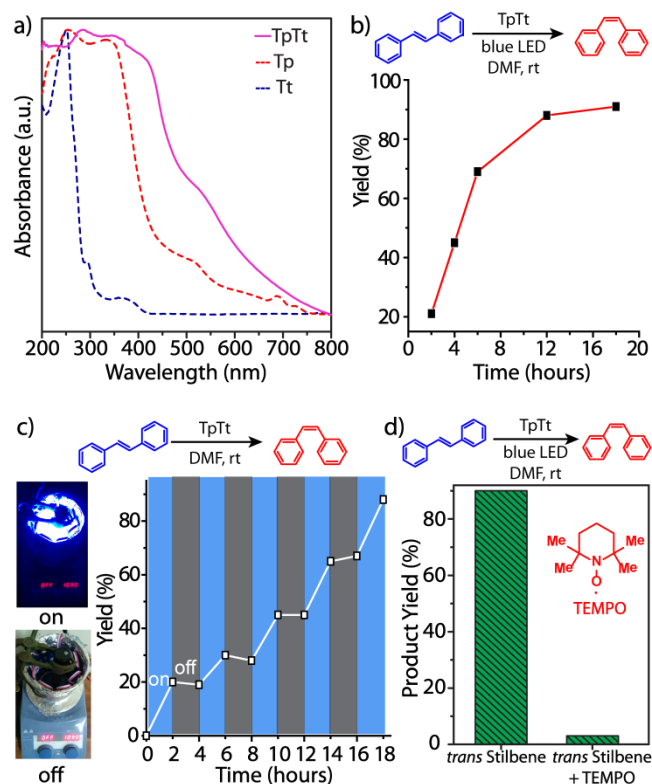


Figure 2. (a) Solid state UV-Vis diffuse reflectance spectra of TpTt (pink), Tp (red) and Tt (blue). (b) The photocatalytic yield of *cis*-stilbene at different time intervals. (c) Light on off experiment study over time. (d) The photocatalytic yield of *cis*-stilbene in the absence and presence of a free radical scavenger (R.S.) TEMPO.

that in the absence of the catalyst, only higher energy UV radiation is necessary for the *trans* to *cis* isomerization process. To prove that the reaction is neither thermodynamically nor kinetically controlled, we have performed the reactions at 80 °C

Table 1. Optimization of the Reaction Conditions.^a

entry	catalyst	temp	solvent	yield[%] ^b
1	TpTt	rt	DMF	90
2	-	rt	DMF	trace
3	Melamine (Tt)	rt	DMF	trace
4 ^[c]	TpTt + TEMPO	rt	DMF	trace
5 ^[d]	TpTt	80 °C	DMF	-
6 ^[d]	TpTt	rt	DMF	-

^aAll reactions were conducted with 0.5 mmol of *trans*-stilbene (1 equiv.), 4 mg TpTt catalyst, in 5 mL solvents at rt under blue LEDs irradiation (total 36 W; each LED has 1 W power) for 18h.

^bBased on GC analysis using n-decane as an internal standard. ^c4 equiv. TEMPO was added into the reaction mixture. ^dIn absence of blue LEDs source.

(Table 1, entry 5) and rt (Table 1, entry 6) in absence of blue LED light. No product (*cis*-stilbene) is formed under these conditions. TpTt has shown good yield towards the *trans* to *cis* photoisomerization of different stilbene substrates (Table 2). The significance of visible light source is essential for this transformation was investigated by performing the light on-off experiment over time (Figure 2c). The reaction proceeds when the light is on, and the conversion stops when the light is turned off, which indicates that the reaction happens through a photocatalytic pathway. To check the recyclability of the TpTt catalyst, we have carried out the photocatalytic activity test up to four cycles. Even after four cycles, the TpTt catalyst showed similar photocatalytic activity (Section S15). The unchanged FTIR, PXRD, TEM and gas adsorption isotherm of TpTt catalyst after 20 hours of photo exposure in DMF suggests the high photostability of the catalyst (Section S17).

Table 2. Porous COF Catalyzed Photoisomerization of Alkene Substrates Scope.^{a,b}

Substrate	Product	Substrate	Product

^aAll the reaction were conducted with 0.5 mmol of *trans*-stilbene (1 equiv.), 4 mg TpTt catalyst, in 5 mL *N,N*-dimethylformamide at rt under blue LEDs irradiation (total 36 W; each LED has 1 W power) for 18h. ^bIsolated yields.

To explore the catalytic reaction mechanism, we have performed a controlled photocatalytic reaction using a radical scavenger (R.S.) TEMPO. In the presence of 4 eq TEMPO R.S. in the reaction medium, the yield of the *cis* product decreases significantly [~3%] under the optimized conditions, which confirms that the reaction proceeds through a biradical intermediate state (Figure 2d, Table 1, entry 4).^{10b-c,11c,18} To get further insight about the reaction mechanism, we have performed theoretical calculations of energy states of different possible reaction intermediates during the isomerization reaction (Section S18). The results indicate that the first TpTt absorbs visible light and gets excited from the ground state to the first singlet excited state (S_0 to S_1). After the intersystem crossing (ISC) TpTt reaches the energetically more stable triplet excited state (T_1) and subsequently interacts with *trans*-stilbene and transfers its energy¹⁹ to the *trans*-stilbene. This energy transfer helps *trans*-stilbene to convert itself into its biradical triplet intermediate state (T_1). This triplet intermediate state then gets converted to the product *cis*-stilbene (Figure 3a).

In conclusion, for the first time, we could successfully develop a heterogeneous TpTt photocatalyst for the visible light-induced isomerization reaction of *trans* to *cis*-stilbene. The hybrid TpTt photocatalyst is synthesized from two types of distinct photoactive building blocks. Due to the β -ketoenamine linked

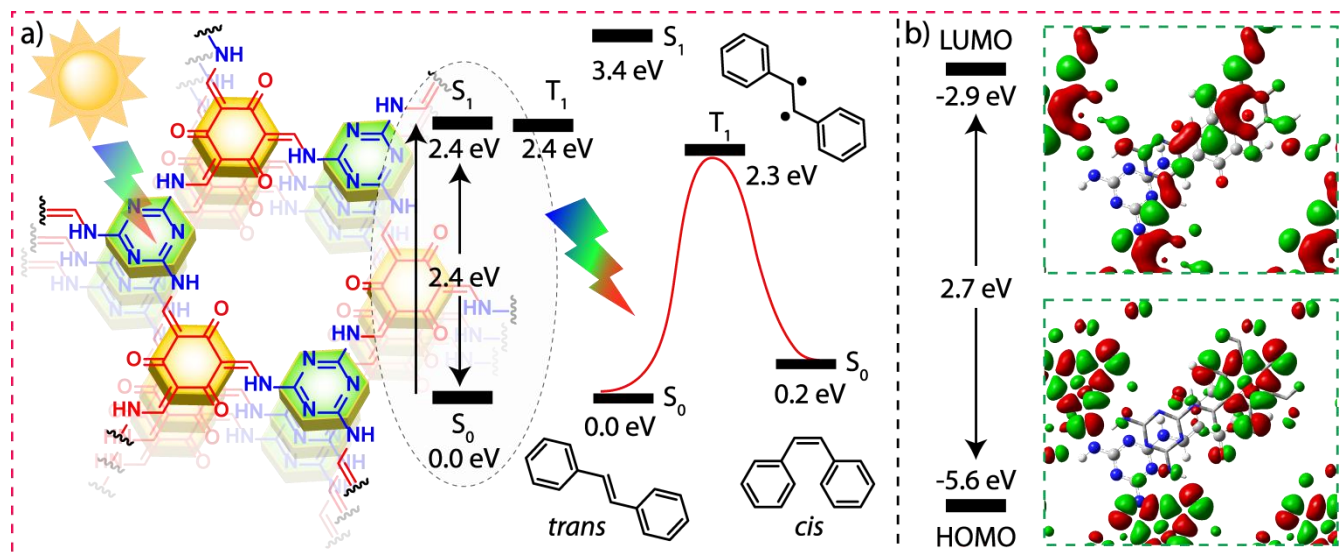


Figure 3. (a) Mechanistic representation of *trans* to *cis* photoisomerization of stilbene using the TpTt COF catalyst. (b) Pictorial representation of HOMO and LUMO orbitals and their energy levels for the TpTt COF catalyst. The energy levels of the orbitals are not exactly to scale.

structure, the novel TpTt catalyst displays high chemical stability even upon irradiation of light and broad substrates scope and retains its photocatalytic activity even after four consecutive reaction cycles. We believe that the novel COF photocatalyst will be a promising candidate for the scalable and cost-effective synthesis of industrially important *cis* olefins.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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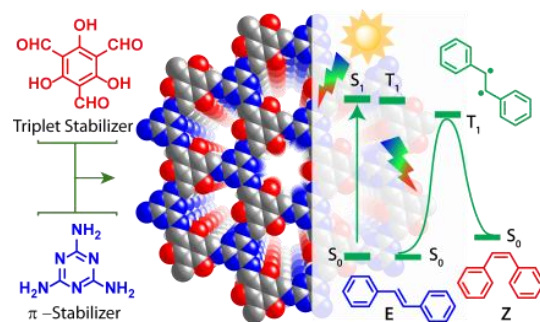
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[**]Although the pictorial representation of both the COFs (COF-TpMA (MC) and TpTi COF) is similar but we believe that our synthesized material has higher crystallinity, porosity, purity and accuracy of the structure prediction from the experimentally observed data compared to the previous report.

Synopsis TOC



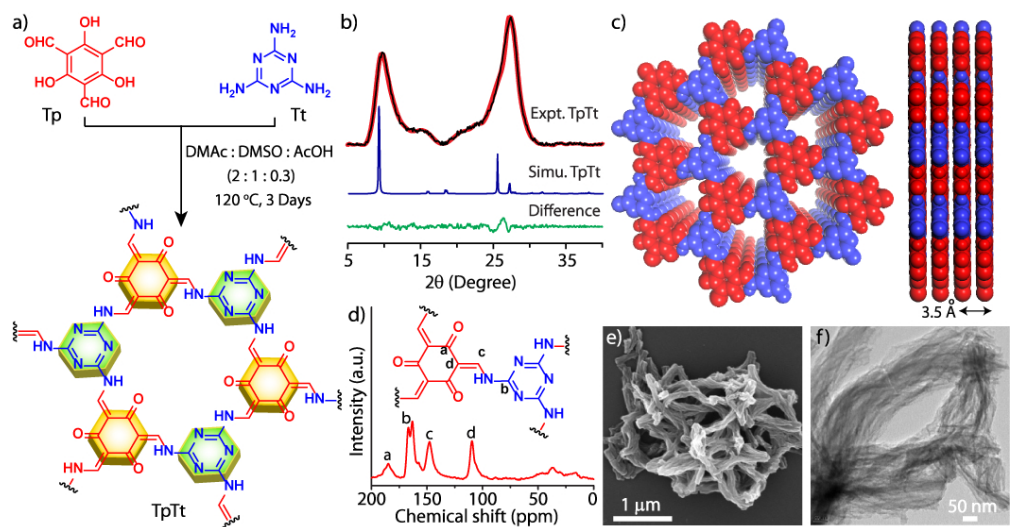


Figure 1

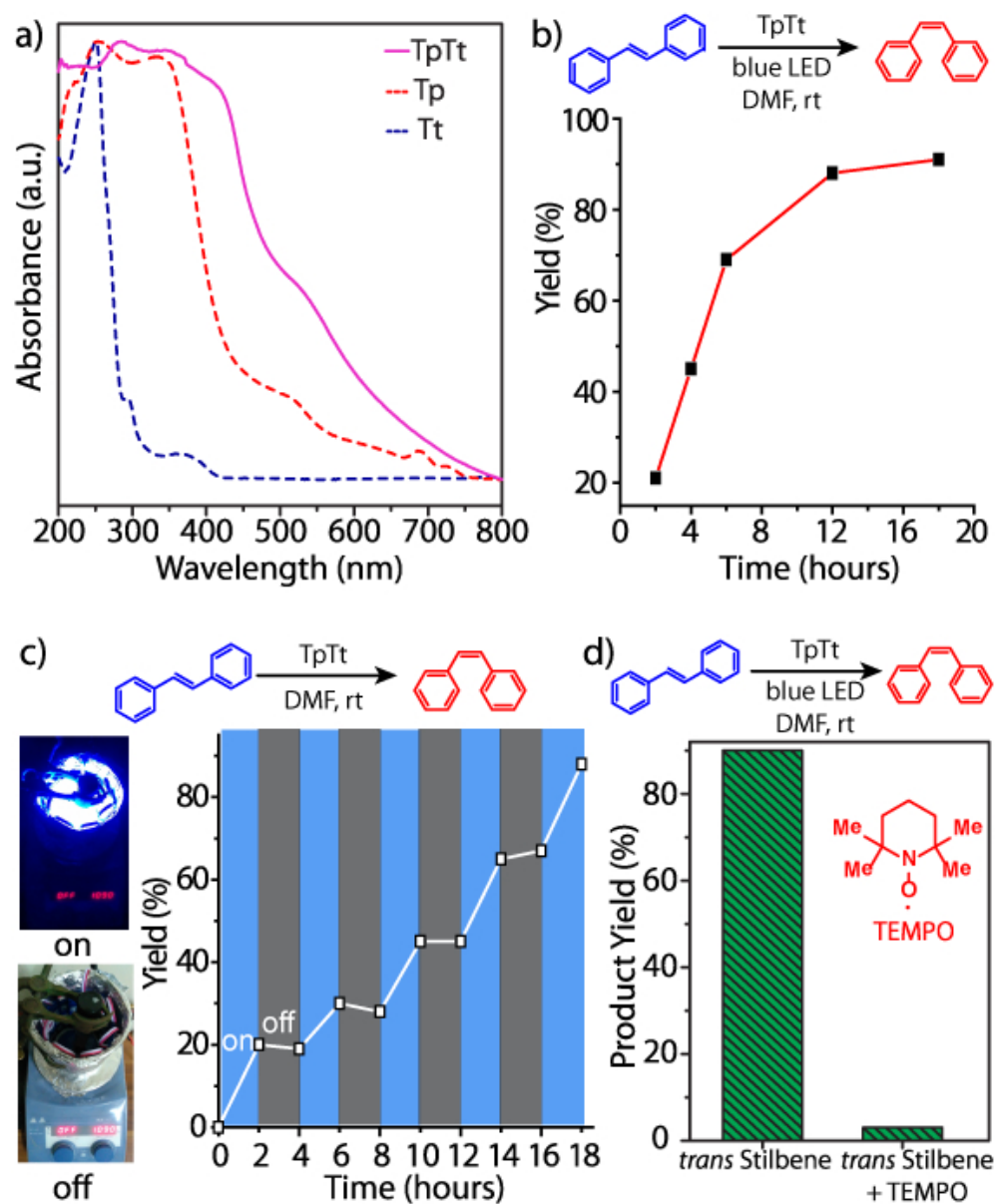
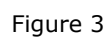


Figure 2



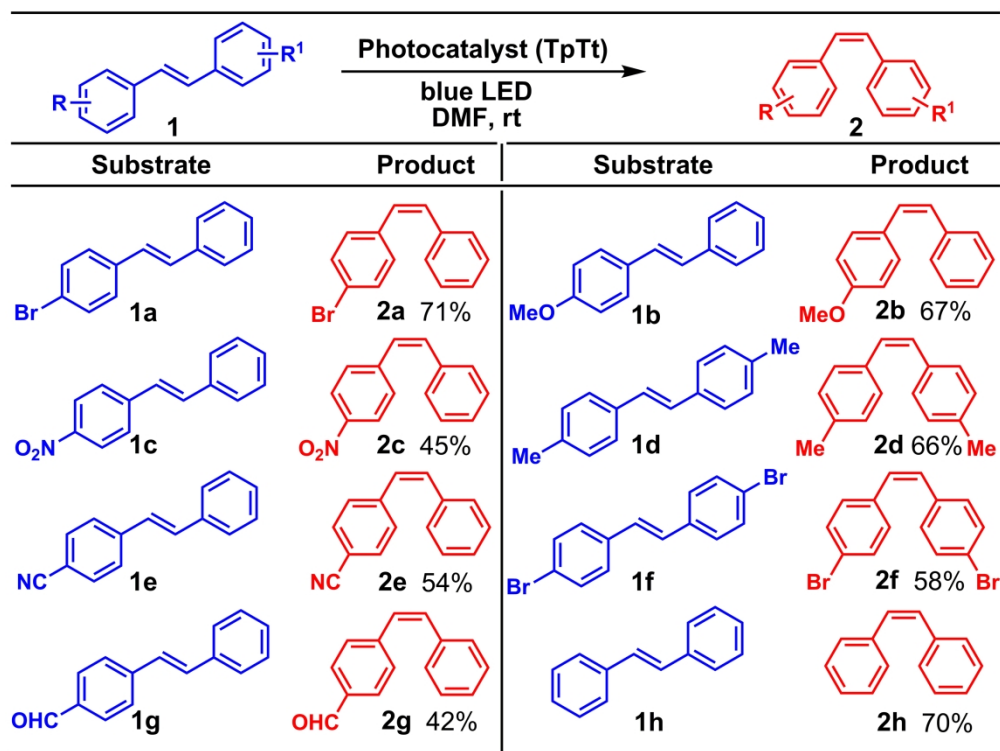


Figure _SubstrateScope

162x122mm (600 x 600 DPI)

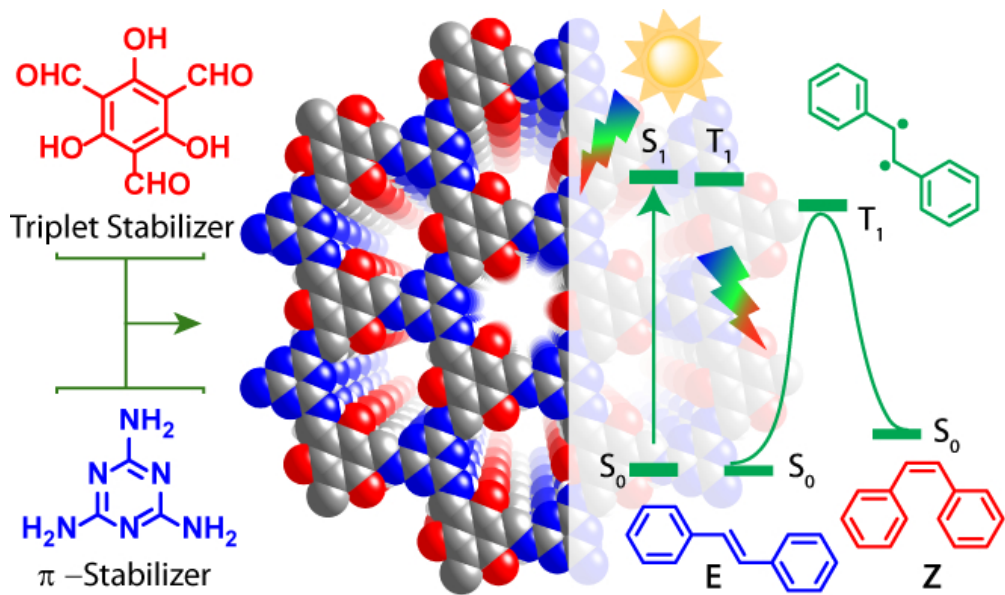


Figure TOC