

Mechanochemical Synthesis of a New Triptycene-Based Imine-Linked Covalent Organic Polymer for Degradation of Organic Dye

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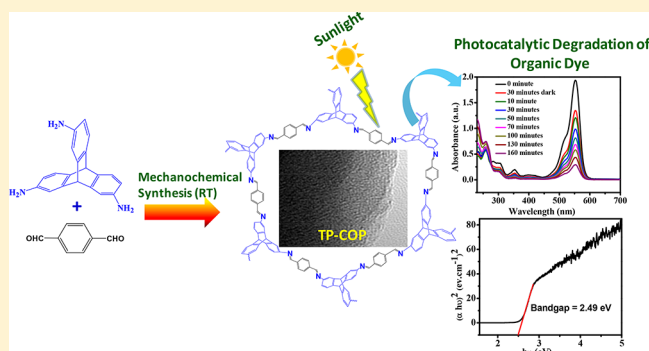
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S Supporting Information

ABSTRACT: In the present work, a novel triptycene-based imine-linked covalent organic polymer (TP-COP) was designed and synthesized via room-temperature, solvent-free mechanochemical grinding. The as-synthesized TP-COP material was fully characterized by Fourier transform infrared spectroscopy, solid-state NMR, field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), Brunauer–Emmett–Teller method, thermogravimetric analysis, diffuse reflectance spectroscopy (DRS), and electron paramagnetic resonance (EPR). The HRTEM image of TP-COP clearly indicates the presence of graphene-like layered morphology (exfoliated layers). The DRS study reveals that TP-COP exhibited a low optical band gap value of 2.49 eV, implying its semiconducting nature. Further, the EPR study confirmed the semiconducting behavior of TP-COP through the generation of free radicals. These findings suggest that TP-COP could be used as an efficient photocatalyst for the degradation of organic dye (RhB) under solar irradiation. Moreover, TP-COP showed excellent reusability in degrading dye (RhB) without obvious performance decay.



Organic dyes have caused severe environmental pollution due to their poor biodegradation. Hence, removal of dye molecules from industry effluent is highly significant for environmental protection.^{1–4} In this context, photocatalysis, as a green approach, has been explored for the degradation of organic dyes.^{5–9} Thus, the development of novel photocatalysts is emerging as a fertile research area to solve environmental issues such as water and air pollution.

In recent years, porous materials such as metal organic frameworks (MOFs),^{10–13} porous coordination polymers (PCPs),^{14,15} porous carbons,^{16,17} covalent triazine-based frameworks (CTFs),¹⁸ and covalent organic polymers (COPs)^{19,20} have extensively been studied for various potential applications. Interestingly, porous carbons, CTFs, and COPs which are linked by strong covalent linkages have been considered as more promising materials than MOFs and PCPs due to their high hydrothermal stability. In particular, among these covalent linked porous materials, COPs with two- or three-dimensional (2D or 3D) network structures that are composed of suitably designed molecular building blocks via covalent linkages to each other demonstrate outstanding

features such as unique ordered structures, relatively large surface area, high chemical and thermal stabilities. Recently, COPs have been intensively investigated as promising materials for gas storage and separation, heterogeneous catalysis, proton conductivity, optoelectronics and energy applications.^{21–30} Interestingly, 2D COPs whose solid-state assembly is driven by electron-rich organic building blocks can exhibit π – π stacking induced high charge carrier mobilities, thus making COPs promising photofunctional materials.^{31,32} Recently, COPs have been explored as photocatalysts for visible light driven hydrogen evolution from water.^{33,34} Although several reports on COPs as photocatalysts toward visible light driven hydrogen evolution have already been made, very few studies have shown the utility of COPs as photocatalysts for the degradation of organic dye pollutants.^{35–37}

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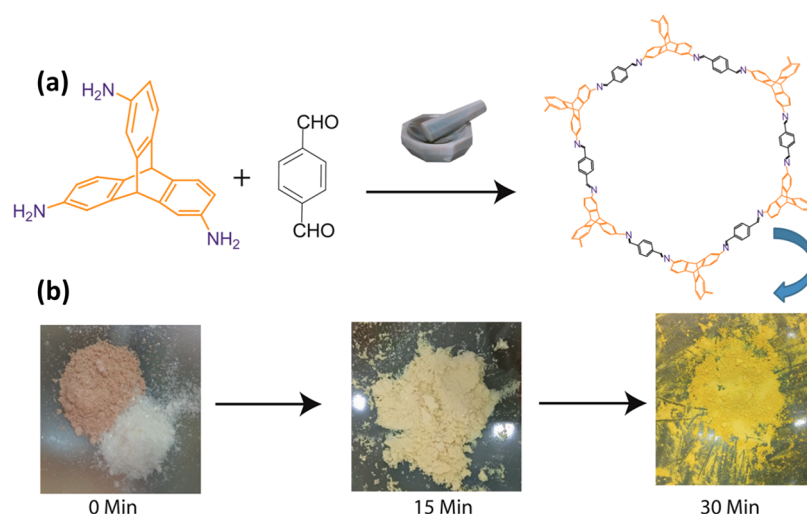


Figure 1. (a) Schematic representation of the mechanochemical synthesis of TP-COP. (b) Optical images of product formation at different time intervals during mechanochemical grinding.

Over the past decade, the syntheses of imine-linked and other nitrogen-containing COPs have been explored through the condensation of aryl amine and aldehydes under suitable solvothermal conditions.^{19,20,31–33,37,38} Furthermore, a mechanochemical approach, which seems to be a promising alternative to the conventional solvothermal methodology, has been efficiently employed to obtain porous organic materials (POMs) such as polymers of intrinsic microporosity (PIMs), CTFs, COPs, and hydrogen bonded organic frameworks (HOFs).^{39–42} In this context, Banerjee et al. explored a simple, solvent-free, room-temperature mechanochemical synthetic route for the construction of imine-linked 2D COPs.⁴¹ However, to the best of our knowledge, mechanochemically synthesized triptycene-based imine-linked 2D COP as an efficient photocatalyst has not been reported to date.

In this work, we report for the first time the rapid, room-temperature, solvent-free mechanochemical synthesis of a triptycene-based imine-linked covalent organic polymer, TP-COP, by manual grinding of the monomers (triaminotriptycene and terephthalaldehyde) in a mortar and pestle (Figure 1). The initial formation of TP-COP was identified by a visual color change and Fourier transform infrared (FTIR) spectra. Interestingly, the synthesized TP-COP material was found to exhibit graphene-like layered morphology (exfoliated layers) which is highly advantageous for the photocatalytic degradation of organic dyes. The optical band gap of TP-COP calculated from DRS implies its semiconducting nature. Further, an electron paramagnetic resonance (EPR) study confirmed the semiconducting behavior of TP-COP through the generation of free radical. Noticeably, the TP-COP was found to act as an efficient photocatalyst toward the decomposition of organic dye (RhB) under sunlight. Importantly, TP-COP showed excellent reusability in degrading dye without obvious performance decay.

In a typical synthesis, triaminotriptycene (1 mmol) and terephthalaldehyde (1.5 mmol) were placed in a mortar and ground using a pestle at room temperature; after 15 min, a light-yellow powder (a mixture of oligomers and starting materials) was obtained (Figure 1). Over the next 30 min of grinding, a powdered material with a deep-yellow color was obtained, indicating the complete TP-COP formation as there was no change in color upon further grinding. The details of

the experimental procedure are provided in [Supporting Information](#).

The formation of TP-COP was confirmed by solid-state ¹³C cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) and FTIR results, as depicted in [Figure 2](#) and [Figure S1](#). The ¹³C CP/MAS NMR spectrum of

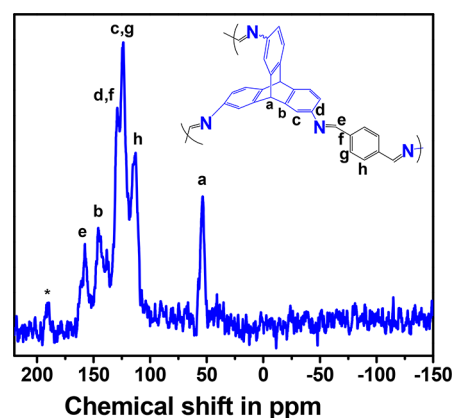


Figure 2. ¹³C CP/MAS solid-state NMR spectrum of the covalent organic polymer TP-COP.

TP-COP displayed six kinds of carbon signals with chemical shifts of 52, 115, 125, 130, 145, and 158 ppm, respectively. Importantly, the peak at 52 ppm could be assigned to the methylidyne bridge carbon (a), while the aromatic carbons of triptycene unit (h, c, g, d, f and b) appeared at 115, 125, 130, and 145 ppm, respectively.^{31,32} In addition, peak (e) at 158 ppm confirms the formation of the imine bond (Figure 2).²⁰ As shown in [Figure S1](#), the disappearance of N–H stretching bands in FTIR spectra of TP-COP compared with that of its precursor monomer (TP-NH₂) demonstrated the formation of C=N bonds (Schiff-base). On the other hand, CH=O stretching band also vanished in FTIR spectra of TP-COP compared with that of its precursor monomer (terephthalaldehyde), further confirming the formation of C=N bonds in TP-COP.

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images were

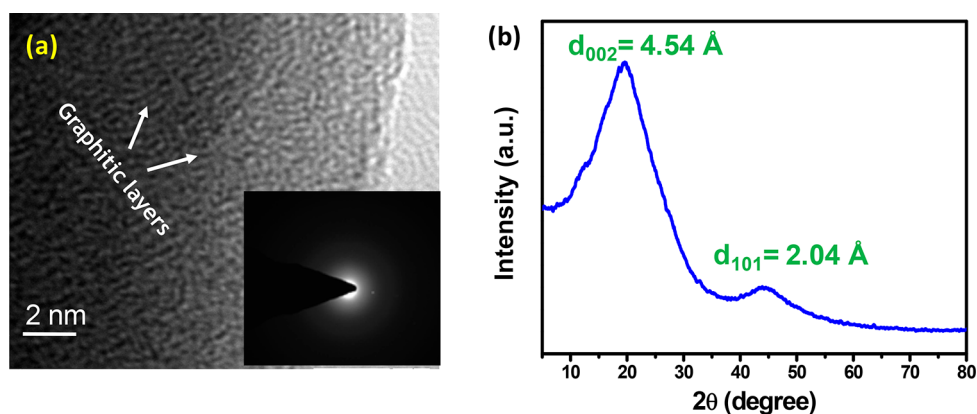


Figure 3. (a) High-resolution TEM image of TP-COP; inset showing the corresponding SAED pattern of TP-COP. (b) Powder X-ray diffraction (PXRD) patterns of TP-COP.

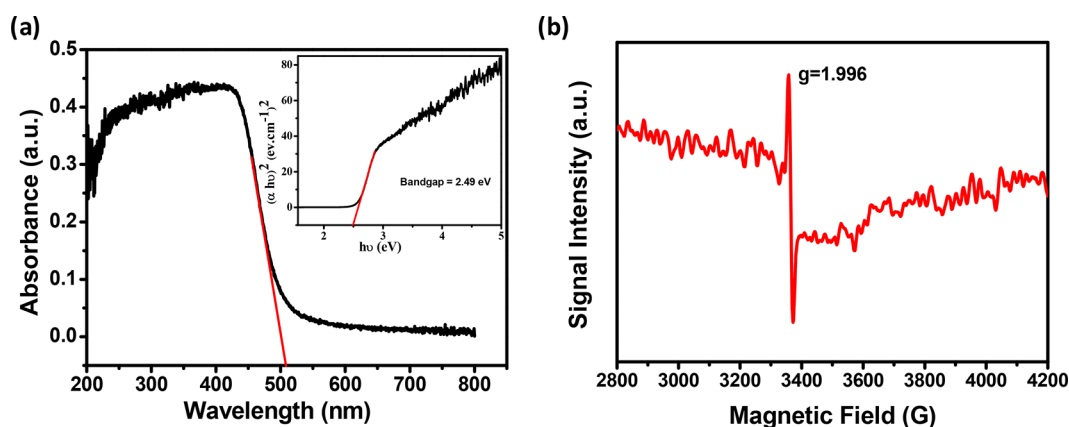


Figure 4. (a) UV-vis DRS spectrum of TP-COP. Inset shows the energy band gap value computed from Tauc's relation. (b) EPR spectrum of TP-COP.

employed to investigate the structural morphologies of the TP-COP, as shown in Figure S2 and Figure 3. FESEM image of TP-COP reveals the formation of sphere-like aggregated particles with a diameter range of 100–200 nm (Figure S2). Further, a low-resolution TEM image of TP-COP indicates the presence of an exfoliated 2D-sheet-like structure (Figure S3a). This finding clearly infers that the strong mechanical force facilitates the exfoliation of 2D sheets of TP-COP.^{41,42} Notably, the high-resolution TEM image clearly indicates the presence of a layered structure of 2D polymer (TP-COP) with low-range order, in accordance with PXRD results (Figure 3b). Additionally, the existence of graphitic-like layers with a spacing of around 0.45–0.46 nm, which is slightly higher than that of graphitic materials ($d_{002} \approx 0.38$ nm), further implies the exfoliation of 2D layers (Figure 3a).¹⁷ In order to understand the crystallinity of the as-prepared 2D TP-COP material, a powder X-ray diffraction (PXRD) pattern was determined as shown in Figure 3b. The PXRD pattern exhibits two broad diffraction peaks at around 19.5° and 43.5° corresponding to the (002) and (101) planes of graphitic-like materials, respectively (Figure 3b).¹⁷ The appearance of broad peaks indicates the low-range crystallinity of the TP-COP material owing to the random displacement of the 2D layers (i.e., exfoliation), which may hinder the pore accessibility. Importantly, the calculated d spacing for the (002) plane is found to be ~ 4.54 Å, which is slightly higher than that of graphitic materials ($d_{002} \approx 3.8$ Å) implying the formation of a more exfoliated structure of the TP-COP material.⁴¹

To investigate the specific surface area (SSA) and porosity of covalent organic polymer (TP-COP), the N_2 sorption isotherm and the pore size distribution (PSD) were analyzed by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively (Figure S4). The BET surface area of TP-COP was determined to be 57.98 cm² g⁻¹, and the total pore volume was 0.12 cm³ g⁻¹. The PSD curve for TP-COP reveals that micropores and small-sized mesopores were found at 1.76, 2.44, and 4.79 nm. Despite the presence of both micro- and mesopores in TP-COP, the BET surface area is low owing to the irregular stacking via mechanochemical grinding, which further supports the PXRD finding.⁴¹

Additionally, for investigating the thermal stability of the TP-COP material, thermogravimetric analysis (TGA) under nitrogen atmosphere was performed. Notably, the as-synthesized TP-COP showed almost no weight loss even up to 420 °C, indicating its excellent thermal stability (Figure S5). Such promising thermal stability is highly beneficial for realistic application toward the exploration of photocatalysis under harsh conditions.

The solid-state diffuse reflectance spectrum (DRS) revealed that TP-COP material absorbs light in the visible region and shows absorption profiles with an absorption edge at ~ 508 nm (Figure 4a), thereby suggesting an optical band gap of ~ 2.49 eV as determined by the Tauc's plot. The optical band gap of TP-COP is lower than that of ZnO (~ 3.45 eV), the most commonly used photocatalyst. Such low optical band gap is

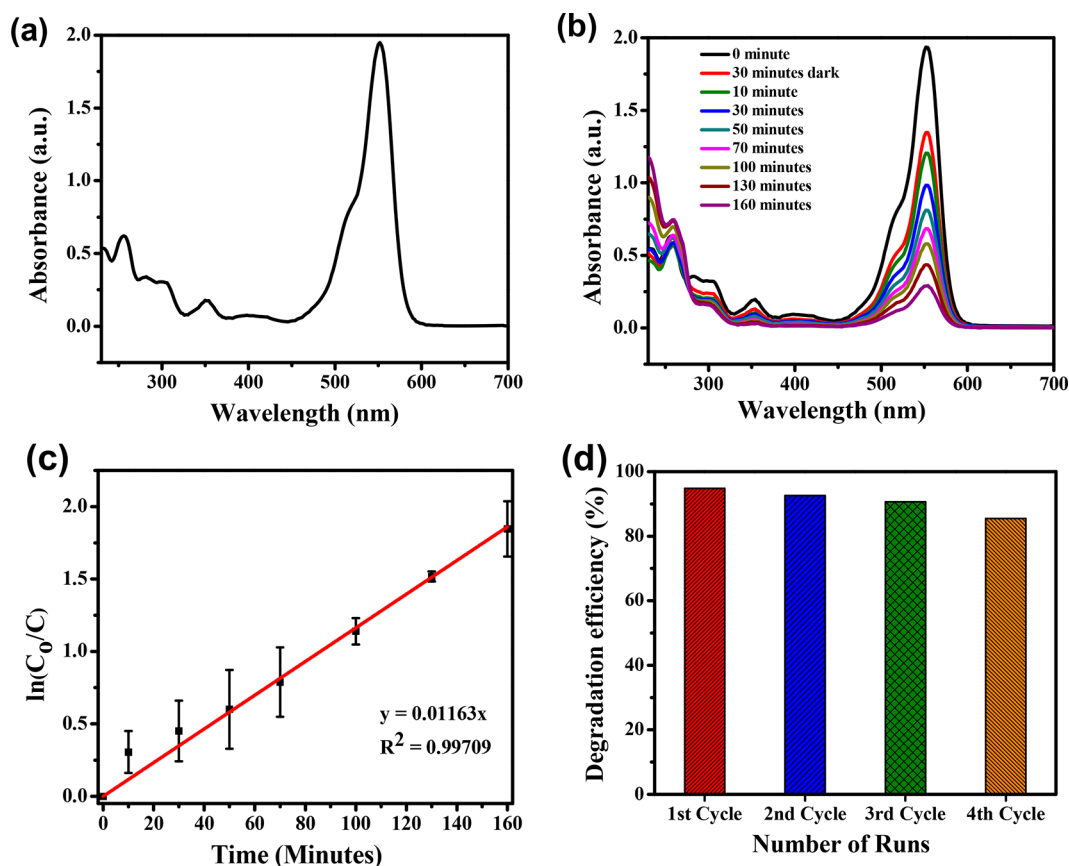


Figure 5. (a) UV-spectra of (pH 4.6, 10 ppm) Rh B dye at λ_{\max} 552 nm, (b) UV-vis absorbance spectra of Rh B dye at natural pH (4.6), catalyst dose (1 g/L), and dye concentration (10 ppm) under sunlight measured at different time intervals. (c) Plot of $\ln(C_0/C_t)$ versus time (min) showing kinetics of photocatalytic reaction (d) % degradation efficiency of observed recyclability.

highly desirable for charge transfer interactions which may lead to the generation of free radicals.^{43,44} Therefore, the EPR spectrum was recorded for TP-COP at room temperature for identifying the generation of charge carriers with unpaired electrons (free radicals).⁴⁵ Figure 4b reveals that TP-COP exhibits a sharp radical signal at around $g = 1.99$ in X-band EPR at room temperature. These findings indicate that the synthesized material has ample potential to be a promising photocatalyst for the degradation of recalcitrant and hazardous organic contaminants under solar irradiation.

The photocatalytic performance of the sample was evaluated by monitoring the degradation of rhodamine B (RhB) dye under solar light irradiation. RhB dye is a basic red dye of xanthene family; it is highly water-soluble dye and is widely utilized as a fluorescent tracer, colorant in textile industries, and in food stuffs in numerous ways. Keeping in mind its toxicological and hazardous effects, it becomes a matter of significant concern to remove RhB from wastewater using appropriate and advanced technologies. The photocatalytic degradation of RhB dye was carried out under sunlight irradiation for about 160 min using TP-COP. The UV-vis absorbance spectra of RhB dye and its photocatalytic degradation at different intervals is shown in Figure 5a,b, and it could be estimated from the graph that the absorbance of dye (10 ppm) at λ_{\max} (552 nm) was found to be continuously decreasing. Within the course of 160 min of photocatalytic reaction under solar light illumination, 95% dye degradation was observed at a natural pH of 4.6 with a catalyst dose of 1 g/L. The kinetic model of photocatalytic reaction

was also estimated by using the Langmuir-Hinshelwood kinetics model equated below: $\ln(C_0/C_t) = kt$, where C_0 and C_t are the concentrations of RhB dye at $t = 0$ and t minutes of photocatalytic reaction, k is the slope of the linear curve representing rate constant of the reaction, and t is the time of the reaction in minutes. Figure 5c shows the Langmuir-Hinshelwood kinetics model showing pseudo-first-order reaction kinetics. The curve linearly fitted with a correlation constant (R^2) 0.99709 with a reaction rate constant to be 0.01163 min^{-1} . Further, the recyclability of the prepared TP-COP catalyst was also investigated by conducting photocatalytic experiments under similar conditions. The photodegradation efficiency observed for RhB dye after the second, third, and fourth cycle was about 93%, 91%, and 85% respectively, which inferred that the prepared TP-COP catalyst possessed significant photocatalytic properties even after the fourth cycle, as shown in Figure 5d. In order to compare the photocatalytic dye degradation of our newly designed mechanochemically synthesized TP-COP with the reported COPs, Table S1 presents the comparative findings.

In summary, we for the first time have designed and mechanochemically synthesized a triptycene-based imine-linked covalent organic polymer (TP-COP) at room temperature. The as-synthesized TP-COP exhibited a graphene-like layered structure with high thermal stability. Notably, DRS and EPR studies reveal the semiconducting nature of TP-COP material through the presence of a low optical band gap ($\sim 2.49 \text{ eV}$) as well as the generation of free radical. The TP-COP material was found to exhibit excellent photocatalytic activities

for the degradation of basic dye (RhB) under sunlight irradiation. Moreover, TP-COP showed remarkable reusability in degrading basic dye (RhB) without obvious performance decay. We anticipate that our findings will provide significant insight toward the development of other semiconducting covalent organic polymers as photocatalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00166.

Experimental procedures and FTIR, FESEM, TEM, BET, PSD, TGA data of TP-COP material (PDF)

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Notes

The authors declare no competing financial interest.

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