Prayogik Rasayan

Triphenylamine-based Donor-Acceptor Conjugated Microporous Polymers in ROS-Mediated Photocatalysis and Pollutant Degradation

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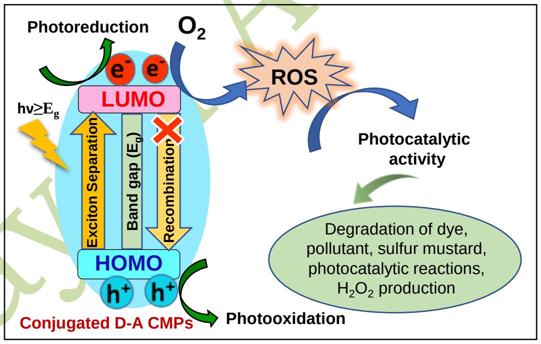
Abstract

Donor-acceptor (D-A) conjugated microporous polymers (CMPs) are an interesting class of molecules for light-mediated generation of various reactive oxygen species (ROS) and photocatalytic organic transformations. We have shown that triphenylamine (TPA) linked D-A CPMs with various acceptor moieties having different acceptor strength, linkage positions, hetero-atom, and fused aromatics are useful in photocatalysis and pollutant degradation. Such D-A CMPs can generate excitons under light and, due to their efficient intramolecular charge transfer (ICT) properties, the excitons can effectively dissociate to produce photogenerated electrons and holes, which can perform reduction or oxidation reactions, respectively. The photogenerated electrons can activate triplet oxygen and reduce it to generate various ROS. These ROS are used for various organic transformations and pollutant degradation towards environmental remediation. We demonstrated that triphenylamine-anthraquinone-based D-A CMPs significantly photogenerate superoxide radical anion ($O_2^{\bullet-}$) for oxidative hydroxylation of phenyl boronic acids to phenols with ~96% yields, as well as photoinduced degradation of micropollutants. Our recent findings demonstrated that single-atom substitution (S→Se) in the acceptor unit can profoundly alter oxygen uptake and charge transfer resistance, key for efficient generation $O_2^{\bullet-}$ for photooxidation of thioanisole. Therefore, this account gives a brief overview of such D-A CMP systems towards photocatalysis.



Keywords: *donor-acceptor, conjugated microporous polymers, photocatalysis, reactive oxygen species, pollutant degradation*

1. Introduction

Donor-acceptor (D-A) based porous organic polymers (POPs) have emerged as promising materials in photocatalysis due to their tunable electronic structures, bandgap, high surface areas, and efficient charge separation capabilities.[1,2] These polymers leverage the strong intermolecular interactions between donor and acceptor units to facilitate charge transfer, thereby enhancing light absorption and catalytic efficiency.[3] By incorporating diverse functional groups, one can tailor their bandgap and optimize redox properties for various photocatalytic applications, including hydrogen evolution, CO_2 reduction, and organic transformations.[4] Also, photocatalytic degradation of toxic micropollutants has innate advantages compared to adsorptive removal, particularly converting them into non-toxic or value-added byproducts.[5] Conjugated porous polymers are photoactive, and upon light exposure, they generate electrons/holes and various reactive oxygen species.[6]

The photocatalytic mechanism in D-A CMPs is fundamentally governed by their π–π* transitions, which generate photoexcited charge carriers (electrons and holes) upon light absorption.[7,8] To enhance the separation efficiency of these photogenerated excitons and suppress recombination, donor–acceptor (D–A) design strategies have been introduced.[9] By rationally incorporating electron-rich donor units and electron-deficient acceptor units within the CMP backbone, a strong internal dipole is established.[10] Upon illumination, this architecture promotes intramolecular charge transfer (ICT) from donor to acceptor, resulting in spatially separated HOMO and LUMO orbitals and significantly improved exciton dissociation. This efficient charge separation facilitates the generation of reactive oxygen species (ROS), such as superoxide ($O_2^{\bullet-}$) and peroxide (O_2^{2-}), which are crucial intermediates in photocatalytic degradation.[11]

2. TPA-based D-A CMPs: Literature Reports

The strategic integration of triphenylamine (TPA)-based donor–acceptor (D–A) segments into conjugated microporous polymers (CMPs) has attracted considerable international attention for their pivotal roles in photocatalytic energy conversion and environmental remediation.[12,13] A growing body of literature from leading global research groups underscores the effectiveness of these moieties in promoting charge separation, enhancing visible-light absorption, and modulating redox properties—key parameters in the development of efficient, metal-free photocatalysts.[14] TPA-based systems have demonstrated exceptional versatility across a range of light-driven transformations, including reactive oxygen species (ROS)-mediated photocatalysis, pollutant degradation, and hydrogen evolution.[15,16]

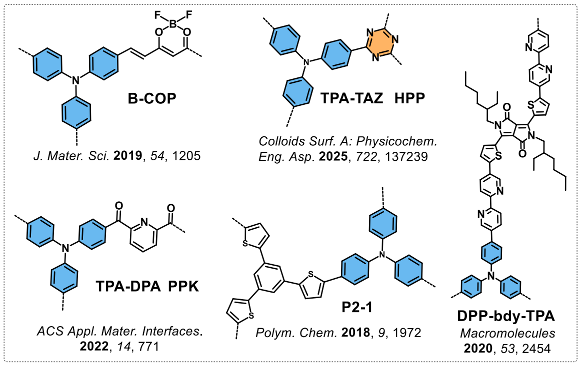
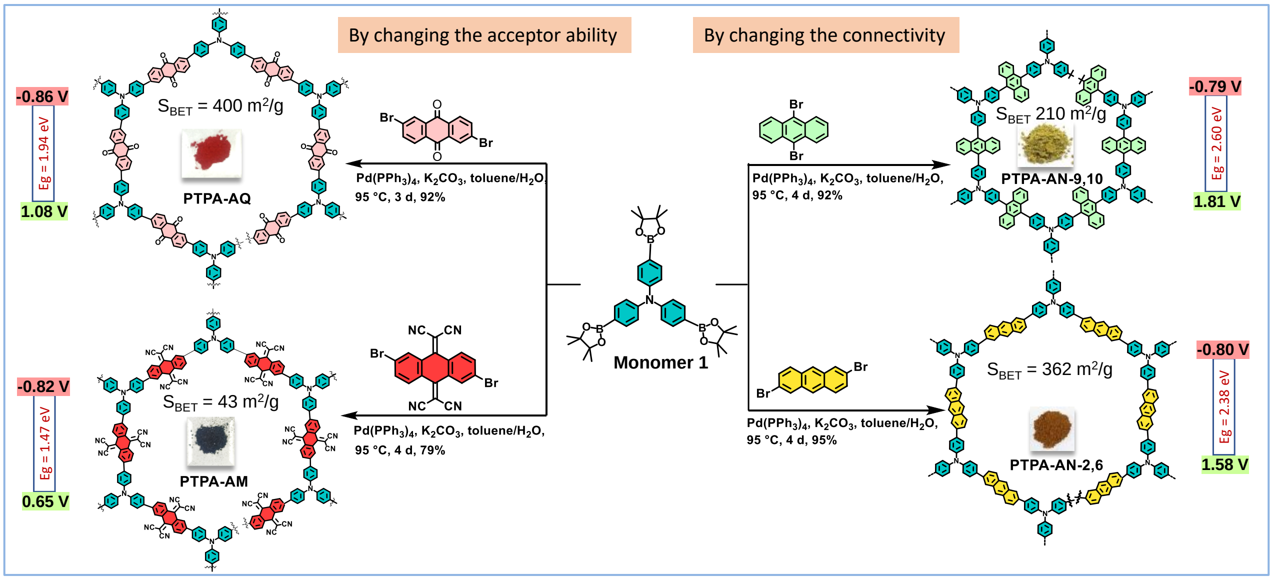


Chart 1. TPA-based D-A CMPs reported in the literature.

In 2019, Liu *et al*. reported a TPA–difluoroborate-based conjugated organic polymer (B-COP) that catalyzed oxidative coupling of primary amines and cross-dehydrogenative coupling reactions under ambient oxygen.[17] This material delivered nearly quantitative conversion (>97%) in a model aza-Henry reaction between *N*-phenyl-1,2,3,4-tetrahydroisoquinoline and nitromethane, achieving high turnover numbers (TON = 3.26–4.85) within 24–36 hours using a 20–30 mol% catalyst loading. More recently, Ejas et al. reported the synthesis of a TPA–triazine-derived hypercrosslinked porous polymer (**TPA-TAZ HPP**) tailored for combined adsorption and ROS-assisted degradation of organic dyes in aqueous media.[16] This material enabled ultra-fast and nearly complete removal (>99%) of rhodamine B (RhB) and methylene blue (MB) within just 5 minutes, exhibiting high adsorption capacities of 951 mg g^{-1} for RhB and 858 mg g^{-1} for MB. Beyond adsorption, it also delivered strong photocatalytic activity, achieving degradation efficiencies of 88% (RhB) and 96% (MB) with rate constants of 5.78×10^{-2} min^{-1} and 9.62×10^{-2} min^{-1}, respectively, highlighting its bifunctional performance in wastewater purification. In the context of hydrogen evolution, Xiao et al. designed a TPA-based donor–acceptor CMP (**DPP-bdy-TPA**), which exhibited outstanding photocatalytic hydrogen production rates of 6918 μmol g^{-1} h^{-1} under full-spectrum light and 2780 μmol g^{-1} h^{-1} under visible-light irradiation (>440 nm), despite its relatively low surface area (17.85 m^2 g^{-1}).[18]

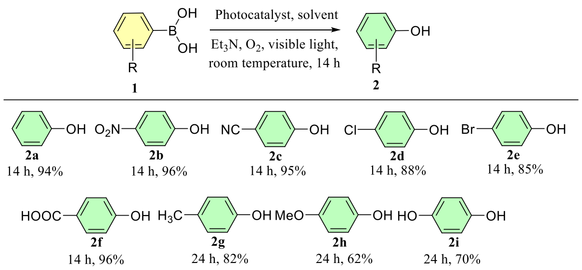
3. Our Results

We have synthesized TPA-based D-A CMPs with anthracene derivatives by altering the acceptor strength and connectivity.[19,20] This not only modulated the band gaps of the generated materials but also altered their porosity drastically. TPA-based D-A CMPs, namely, **PTPA-AQ** and **PTPA-AM** (Scheme 1), were synthesized *via* Suzuki–Miyaura cross-coupling of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-amine as a donor with 2,6-dibromoanthracene-9,10-dione and 2,2′-(2,6-dibromoanthracene-9,10-diylidene)dimalononitrile acceptors with high yields.[13] Both of these D-A CMPs showed visible-light-driven superoxide radical anion ($O_2^{\bullet-}$) generation, which was utilized for the efficient visible-light-driven oxidative hydroxylation of several phenylboronic acid derivatives. **PTPA-AQ**, with a higher Brunauer–Emmett–Teller (BET) surface area (400 m^2 g^{-1}), favorable HOMO–LUMO alignment, and an optimal band gap of 1.94 eV, demonstrated superior photocatalytic performance, achieving yields of up to 96%. Such high yields were obtained for various substrates (Table 1). On the other hand, the dimalononitrile derivative has greater acceptor ability and thus **PTPA-AM** showed a lower band gap of 1.47 eV and porosity (BET surface area of 43 m^2 g^{-1}), which are responsible for its lower yields.



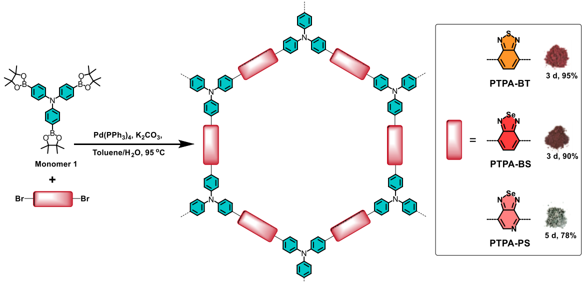
Scheme 1. TPA-based D-A CMPs with anthracene derivatives by altering the acceptor strength and connectivity.

Table 1. Visible-light-driven oxidative hydroxylation of substituted phenylboronic acids.



[a]*Reaction conditions:* Substituted phenylboronic acid (0.25 mmol), **PTPA-AQ** polymer (5 mg), Et_3N (0.375 mmol), CH_3CN (2 mL), O_2, room temperature, white LED (18 W). Product yields were determined based on the isolated compounds.

Following a similar approach, TPA–anthracene-based D-A CMPs, **PTPA-AN-9,10** and **PTPA-AN-2,6** were prepared Scheme 1) by varying the linkage positions of anthracene derivatives.[14] **PTPA-AN-2,6** showed a higher BET surface area of 362 m^2/g, as compared to **PTPA-AN-9,10** (BET surface area of 210 m^2/g). Their photoactivity was checked towards light-mediated photodegradation of various micropollutants. **PTPA-AN-2,6** showed facile photoreduction of various nitroaromatic pollutants, including *p*-nitrophenol, via the generation of photoelectrons and photodegradation of Congo red dye via the generation of ROS, superoxide radical anion ($O_2^{\bullet-}$). On the other hand, a bright cyan fluorescence was observed in the case of **PTPA-AN-9,10** in tetrahydrofuran dispersion, which was utilized for the fluorescence-based sensing of various nitroaromatic compounds. This showed a lowest limit of detection of 34 µM for 2,4,6-trinitrophenol along with the highest Stern−Volmer constant (K_{SV}) of 5.8×10^3 Lmol^{-1}.

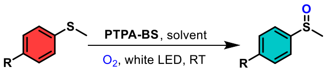


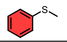
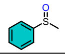
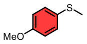
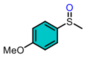
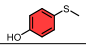
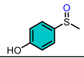
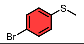
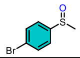
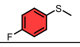
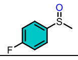
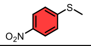
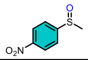
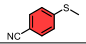
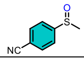
Scheme 2. TPA-based D-A CMPs following two-fold single atom substitutions.

Within a similar TPA-based donor–acceptor CMP platform, even the substitution of a single atom can markedly tune the optoelectronic characteristics. Consequently, dual atomic substitutions (S → Se and C → N) are expected to strongly influence the band gap, conductivity, and charge-carrier dynamics, thereby modulating the photocatalytic performance.[21] In this work, we prepared three isostructural TPA-derived D–A CMPs, namely **PTPA-BT**, **PTPA-BS**, and **PTPA-PS**—incorporating 2,1,3-benzothiadiazole, 2,1,3-benzoselenadiazole, and [1,2,5]selenadiazolo[3,4-c]pyridine units as electron acceptors, respectively. Among them, **PTPA-BS** (C, Se) exhibited the best photocatalytic activity in the visible-light-driven oxidation of thioanisole, achieving >99% conversion with ~93% isolated yield. This superior activity is ascribed to its reduced interfacial charge-transfer resistance, enhanced photocurrent generation, suitable band gap, and improved capability for superoxide radical formation.[21] Moreover, **PTPA-BS** exhibited broad substrate scope, delivering isolated yields ranging from 45% to 97% (Table 2).

Table 2. Substrate scope for the photooxidation of thioanisole

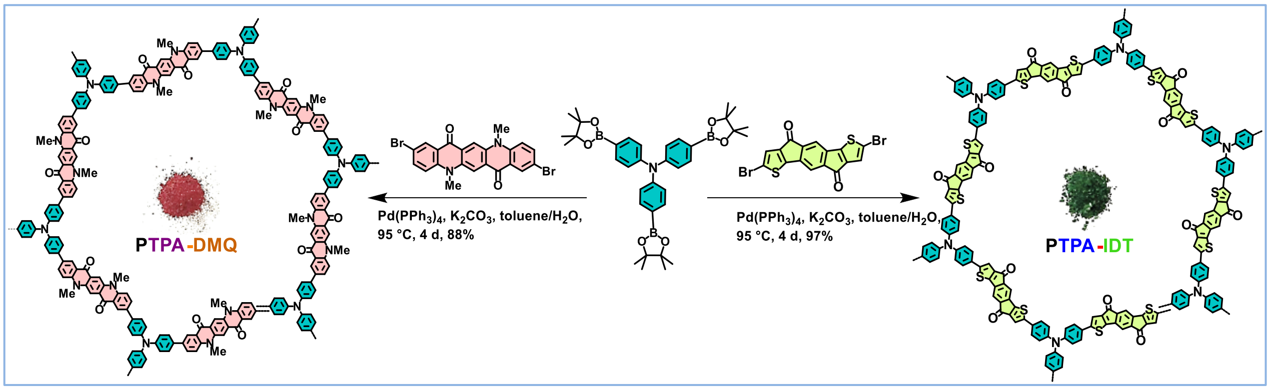
derivatives[a]



Entry	Substrate	Product	t (h)	Yield[b] (%)
1			12	93
2			12	91
3			12	97
4			18	80
5			30	90
6			20	72
7			24	45

[a] Reaction conditions: 0.2 mmol thioanisole, 2 mg **PTPA-BS**, 2 mL MeOH, 1 mL H_2O, a 100 W white LED at room temperature, O_2. [b] Isolated yield.

Building on a similar platform, and expecting better photocatalytic efficiencies from the sulfur-rich, fused aromatic moieties, two TPA-based donor–acceptor CMPs, designated as **PTPA-IDT** and **PTPA-DMQ**, were developed by integrating s-indaceno[1,2-b:5,6-b′]-dithiophene-4,9-dione (IDT) and N,N-dimethylquinacridone (DMQ) moieties into the CMP backbone for the first time.[22] Surprisingly, these D-A CMPs did not show photocatalytic activity towards several organic transformations including ROS-mediated dye degradation, oxidative hydroxylation of phenylboronic acid to phenol, photooxidation of thioanisole, and the pinacol C–C coupling reaction. Interestingly, alteration of the building blocks, led to the modulation of their porosity and morphological features responsible for their enhanced adsorption capabilities. **PTPA-IDT**, characterized by its nanofibrillar morphology and high surface area, exhibited outstanding adsorption performance, achieving maximum uptake capacities of 241.5 mg/g for methylene blue (**MB**), 125.3 mg/g for rhodamine B (**RhB**), and 3.87 g/g for iodine vapor.[22]



Scheme 3. TPA-based D-A CMPs from the sulfur-rich, fused aromatic moieties.

4. Conclusions and Future Perspectives

Environmental pollution arising from organic contaminants, heavy metals, and plastic residues continues to pose a severe threat to ecosystems and human health. Traditional remediation technologies often address these pollutants in isolation, frequently requiring significant energy input and resulting in secondary waste streams. There is an urgent need for integrated, sustainable, and multifunctional catalytic systems that can operate efficiently under ambient conditions and with minimal environmental footprint. Photocatalysis, particularly under visible light, offers a green, solar-driven pathway for pollutant degradation and value-added chemical production. However, many state-of-the-art photocatalysts still rely heavily on precious or toxic transition metals, exhibit limited light-harvesting capability, and suffer from inefficient charge separation and poor long-term stability. These limitations restrict their practical utility, especially for broad-spectrum environmental applications.

In this context, donor–acceptor (D–A) conjugated porous organic polymers (POPs), notably conjugated microporous polymers (CMPs), offer a promising alternative. Their all-organic, metal-free composition, high surface area, extended π-conjugation, and modular structural tunability provide an ideal platform for tailoring photocatalytic behavior. TPA-based D-A CMPs are proven to be highly photoactive and excellent in photocatalytic organic transformations. Strategic incorporation of electron-rich donor units and electron-deficient acceptors—further enhanced by heteroatoms such as N, S, and P—enables precise control over bandgap, redox potentials, and surface interactions, making these materials highly suitable for pollutant adsorption, ROS generation, and metal ion capture.

Despite the rapidly growing interest in this area, very few studies have systematically developed bandgap-engineered, metal-free, multifunctional CMPs capable of simultaneously enabling pollutant degradation, uranium sequestration, and green oxidant generation. Existing literature predominantly addresses these functions in isolation, often using structurally complex or metal-containing systems. In the future, this critical research gap can be addressed by developing a new generation of heteroatom-rich D-A CMPs with broad-spectrum photocatalytic functionality under visible light. This effort is grounded in cutting-edge structure–property design principles and aims to deliver tangible advancements in the following high-impact domains:

(i) Advanced Water Treatment: Adsorption and ROS-mediated photocatalysis will enable efficient removal of persistent organic pollutants and nuclear waste (uranium, UO_2^{2+} and iodine) offering viable solutions for environmental remediation.

(ii) Green Hydrogen: The exciton dissociation in the electron-rich D-A CMPs would enable green hydrogen generation.

In summary, it bridges advanced materials design with real-world applications, offering scalable, metal-free, and multifunctional photocatalysts that can contribute meaningfully to clean water, green chemistry, and circular economy goals.

5. Acknowledgements

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