

Synthesis of an extended organic material with photocatalytic activity through [2+2] photocycloaddition via monomer truncation strategy.

Giacomo De Crescenzo¹, Beatriz de Santos,¹ M. José Capitán,^{2,3} Jesús Álvarez,^{3,4,5,6} Alberto Fraile,^{1,7} Matías Blanco^{1,7} and José Alemán^{1,7}

¹Organic Chemistry Department, Universidad Autónoma de Madrid, 28049 Madrid, Spain

²Instituto de Estructura de la Materia IEM-CSIC, c/ Serrano 121, 28006 Madrid, Spain.

³Física de sistemas crecidos con baja dimensionalidad, UAM, Unidad Asociada al CSIC por el IEM

⁴Condensed Matter Physics Department, Universidad Autónoma de Madrid, 28049 Madrid, Spain.

⁵Instituto de Ciencia de Materiales "Nicolás Cabrera", Universidad Autónoma de Madrid, 28049-Madrid, Spain.

⁶Instituto de Física de la Materia Condensada IFIMAC, Universidad Autónoma de Madrid, 28049-Madrid, Spain ⁷Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain

giacomo.decrescenzo@uam.es

The construction of extended organic polymers such as COFs, POPs or HCPs has been largely achieved via the use of linkages obtained in a polar-thermal manner (i.e. imines, boronate esters, amides, triazines...),[1] but the photochemical synthesis of this class of materials has been however very rarely exploited.[2],[3] Herein, we report the synthesis of two novel extended organic polymer employing a photochemical pathway based on a [2+2] photocycloaddition polymerization of electron-poor olefins, where the monomers shall be linked by cyclobutane moieties. Furthermore, we achieved the heterogenization of an organic photoredox catalyst, *N*-Phenylphenothiazine (PTH), via monomer truncation strategy.[4] The materials obtained were fully characterized both structurally (FTIR Spectroscopy, SS-NMR, XRD, SEM-EDX, XPS) and optoelectronically (UPS, UV-Vis DRS), confirming the formation of the expected cyclobutane linkages. In addition, the truncation introduced up to 10 mol% of the photoactive unit PTH, and the functionalization was observed to be homogeneous throughout the material, showing the compatibility of the photosynthetic method with the monomer truncation strategy. Both the pristine and the PTH-decorated materials were tested as photocatalysts for the oxidative homocoupling of benzyl amines. Interestingly, the introduction of the PTH unit boosted the photocatalytic activity, reaching up to 75% conversion for the oxidation of the model substrate benzylamine *versus* the 45% achieved using the pristine material. Moreover, the truncation improved the stability and robustness of the material under reaction conditions, affording better results in the recycling experiments, reaching 5 cycles without any loss in activity. The catalyst was also found to be versatile and tolerant to a variety of functional groups tested as substituents in the aryl amines

rings, allowing to expand the scope of the catalysis to up to 10 examples. Finally, the PTH-decorated material was also able to catalyze the reductive dehydrohalogenation of 5 different aryl and alkyl bromides. Hence, this work explores the unprecedented photochemical synthesis of an organic polymer which exhibits a versatile activity as a photocatalyst.

References

- [1] A. López-Magano, S. Daliran, A. R. Oveisi, R. Mas-Ballesté, A. Dhakshinamoorthy, J. Alemán, H. Garcia, R. Luque, *Adv. Mater.* 2023, 35, 2209475
- [2] Wu, C.-J.; Li, X.-Y.; Li, T.-R.; Shao, M.-Z.; Niu, L.-J.; Lu, X.-F.; Kan, J.-L.; Geng, Y.; Dong, Y.-B, *J. Am. Chem. Soc.* 2022, 144, 41, 18750–18755
- [3] Wang, G.-B.; Wang, Y.-J.; Kan, J.-L.; Xie, K.-H.; Xu, H.-P.; Zhao, F.; Wang, M.-C.; Geng, Y.; Dong, Y.-B *J. Am. Chem. Soc.* 2023, 145, 9, 4951–4956
- [4] Daliran, S.; Blanco, M.; Dhakshinamoorthy, A.; Oveisi, A. R.; Alemán, J.; García, H. *Adv. Funct. Mater.* 2023, 2312912.

Figures

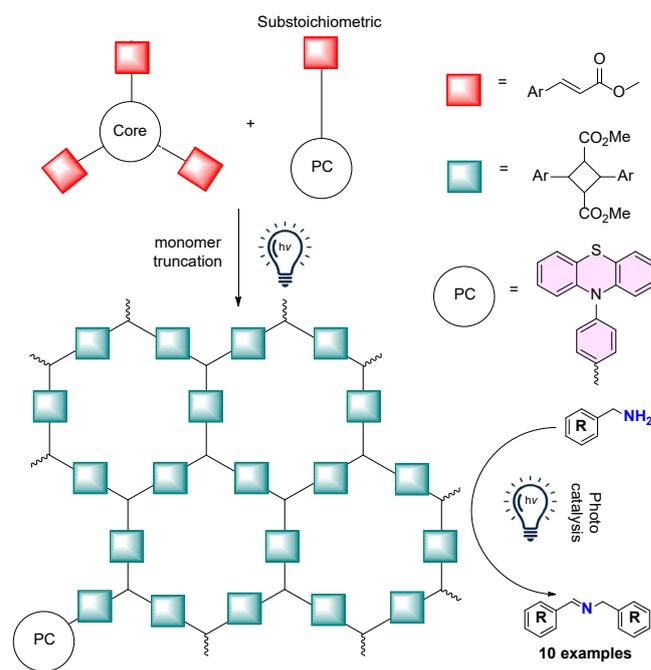


Figure 1. Idea's conceptualization within the light-driven [2+2] polymerization, truncation and photocatalytic activity.