Title:	Designing of Heptazine and Triazine based Porous Organic Polymeric Networks and their applications
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Abstract:	PhD Thesis Title Designing of Heptazine and Triazine based Porous Organic Polymeric Networks and their applications Abstract The research on developing functional materials as a solution to the growing energy demand and environmental remediation is of high importance. Especially, the development of sustainable material which is heterogeneous in nature can help in solving energy and environment related problems. Among the other intensely investigated systems, porous organic polymers (POPs) have shown their versatility in wide variety of applications. POPs can be defined as multidimensional porous polymeric networks with high thermal and chemical stability. The stability of POPs depends upon the building units (linkers or tectons), which further plays an important role in determining the topological property which additionally enhances the property of the system. From the literature, it's well-known that carbon-nitride based polymers are highly stable in untoward conditions and can be explored in multifarious applications. Such application diversity of carbon-nitride based polymers arise due to the presence of exceptionally stable basic structural units, i.e., Heptazine (Tri-s-triazine) and Triazine. Heptazine is one of the oldest known organic moieties in the scientific community, but due to the absence of soluble derivative its least explored until 2009. Heptazine came into limelight as Pauling's "mystery molecule", as a molecular structure, 2-azido-5,8-dihydroxy- 1,3,4,5,7,9,9b-hepta-azaphenalene, having a heptazine core retained on his chalkboard just before his demise. In 1940, Redemann and Lucas, first synthesized the first soluble moiety in trichloro-s-heptazine through a solid phase reaction by reacting K-melem/cyameluric acid with PCl5. After a very long pause, Edwin Kroke in 2002 gave detailed structural studies withextensive characterization data of trichloro-s-heptazine. More precisely, synthesis of three fused aromatic rings of heptazine and their further derivatization to useful molecular compounds would require a starting heptazine core which could be functionalized through known organic synthesis protocols. Thus the synthesis of trichloro-s-heptazine (TCH) made a phenomenal breakthrough which has made synthesis of several compounds and polymer networks feasible thereafter. Since then, few of different heptazine based molecular compounds and polymeric networks were synthesised which were used in different applications (OLEDs, (photo)catalysis, CO2 sorption and conversion, etc). Under this tutelage, we have designed different heptazine and triazine based polymeric networks and used in different applications. Firstly, we have synthesized the heptazine based polymeric network HMP-TAPA by using trichloro-s-heptazine and Tris-(4-aminophenyl) amine as a building unit and achieved a surface area of 424 m 2 /g, which was highest among all earlier known heptazine based polymeric networks. HMP-TAPA exhibited a conversion of 94% with 98% of selectivity for benzyl amine homocoupling under visible light irradiation at room temperature. In addition, the Lewis basic character due to high nitrogen content of the polymeric network is scrutinized for the Knoevenagel condensation reactions of benzaldehyde with methyl cyanoacetate resulting in > 99% conversion to yield α, β-unsaturated ester. We also explored the triazine moiety where we developed triazine based polymeric network TMP-TAPA with Tri-(4-formyl phenoxy) cyanurate and Tris-(4-aminophenyl) amine as building units. TMP-TAPA was used as robust photocatalytic system for cross- dehydrogenative C-C coupling reaction, i.e., Aza Henry reaction. The photocatalytic performances of TMP-TAPA for cross-dehydrogenative coupling have been found achieve about 70% conversion with 99% selectivity of the coupled products. In addition, themechanistic pathways of the reaction have been thoroughly investigated which was further corroborated by controlled studies in addition to scavenger and substrate studies. Controlled experimental studies proposed the formation of singlet oxygen during the reaction which plays the important role in cross-dehydrogenative coupling reaction. Meanwhile, owing to the presence of more basic sites in HMP-TAPA, we used it for the conversion of CO2 into cyclic carbonate for the first time. The catalytic activity of HMP- TAPA was scrutinized for efficient cycloaddition of CO2 with different epoxides at relatively mild conditions and recyclable which was carried out for 5 cycles. HMP-TAPA being rich in nitrogen site showed high CO2 uptake 106.7 mg/g with IAST selectivity of 30.79 towards CO2 over N2 at 273 K, which is highest among the heptazine based porous polymeric networks reported so far. Lastly, we have developed heptazine based polymeric network HMP-TAPB by using trichloro-s-heptazine and Tris-(4-aminophenyl) benzene as building units. HMP-TAPB was used as chemiresistive sensor for ammonia detection at room temperature under ambient conditions. The chemiresistive sensor performance for ammonia was investigated over a wide concentration range (1-200 ppm) and in the presence of a relative humidity range (23-85 %RH). The presence of active sites (C-N and NH groups) and the porous network of a heptazine gas sensor enables an enhanced response (16.6 at 70 %RH and 47 at 84 %RH) towards 50 ppm of ammonia with response and recovery times of 65 and 9 s, respectively. The paramount performance of the present heptazine based porous sensor in selectivity, sensitivity, recovery, stability at room temperature and ambient conditions pace out avenue towards portable hand-held devices or wearable sensors for futuristic sensing applications.In summary, we have designed heptazine and triazine based polymeric networks and utilized them in different applications i.e. (photo)catalysis, cross dehydrogenative coupling reaction, CO2 sorption and conversion and ammonia sensing. In my thesis work, we have demonstrated that the heptazine based porous organic polymeric networks (HMPs) with different donor and acceptor building unit provides an opportunity for wide variety of organic conversions (both as organophotocatalysis and organobase catalysis) to be carried out in the near future.
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