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Highly regioselective and sustainable solar click reaction: A new Post-synthetic modified triazole organic polymer as recyclable photocatalyst for regioselective azide-alkyne cycloaddition reaction

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Dolly Yadav,[a] Nem Singh,[a] Tae Wu Kim,[b] Jae Young Kim,[a] No-Joong Park[a] and Jin-Ook Baeg*[a]

The synthesis of pharmaceutically active 1,2,3-triazoles is been continuously scrutinized in search of a unique and effective catalysts to make the process efficient, green and sustainable. Here we are presenting a new visible light active Ni(II) cyclam integrated triazole linked organic polymer (Ni-TLOP) photocatalyst for the synthesis of 1,2,3-triazoles compounds with absolute efficiency and regioselectivity. The reaction was studied for a series of substrates and the absolute regioselectivity of a representative triazole product has also been conferred by x-ray crystallography. The proficiency and chemical orthogonality of the Ni-TLOP is remarkable and shows enhanced efficiency, regioselectivity. The use of recyclable photocatalyst and non-hazardous reagents makes the catalytic system sustainable and environmentally-friendly. This photo catalyzed click reaction technique has been successfully applied to the expedient synthesis of one of the most selling antiepileptic drug rufinamide.

Introduction

Harvesting visible light for the synthesis of value added chemicals has continuously been a hot topic of research for chemists.[1-3] In this regard a series of homogeneous and heterogeneous photocatalysts have been described with special features to attain maximum efficiency, selectivity, conversion and stability.[4-5] Homogeneous catalysis is undoubtedly on the central theme of the synthetic chemistry but issues such as reusability of the catalyst, tedious product isolation and cost-effectiveness are significant drawbacks that need to be resolved.[6] In contrast, heterogeneous photocatalysis, mainly consisting of semiconductors or metal oxides, has been recognized as an alternative way to compensate stability and harsh reaction conditions, but suffer from selectivity and prolonged reaction time.[7] Covalent organic polymer materials (COPMs) are an emerging class of functional material for their potential applications in the field of heterogeneous photocatalysis.[8-10] Their structural amenability and synthetic tunability provide an appealing and precise platform for development of catalyst with desired catalytic properties.[11-18] COPMs have also shown a great potential in post synthetic modifications to get a range of desired properties by incorporating metal chelating sites or active functional groups. [19-23] Perylene derivatives are widespread visible light absorbing compounds, which are employed in covalent functionalization of polymers and nanomaterials.[24] Post-synthetic modified polymeric materials show interesting applications due to their specific characteristics such as porous or laminar structure with accessible pores, low density and high surface area.[25]

The 1,2,3-triazole scaffold is an integral part of a large number of drugs which are among the bestselling pharmaceutical products. The huge demand of triazole based compounds makes their synthesis a sizzling topic of research for chemists.[26-31] The synthesis of triazole has been investigated for Cu, Ru, Au or Ag metal catalyzed reactions.[3, 27-31] however Ni(II), although being an active center in many catalysed and photo catalysed reactions has not been comprehensively explored.[26d] Most of these click reaction process have their own necessities such as additional suitable bases (TEA, DIPEA, K_2CO_3 etc), different solvents, harsh reaction conditions, modified substrates, and catalysts.[32] The homogeneous metal catalysed process requires the isolated product to be treated with harmful quadrapure thiourea as a copper-scavenging resin in order to demetallate the final compound.[33,34] Moreover, the use of strong base or highly reactive additives make the process functional group intolerant in multi-step synthesis. In this regard, click chemistry has always been a continuous field of

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[a] *Artificial Photosynthesis Research Group, Korea Research Institute of Chemical Technology (KRICT), 100 Jang-dong, Yuseong, Daejeon 34114, Republic of Korea E-mail:jobaeg@krict.re.kr.*
[b] *Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 34141, Korea.*

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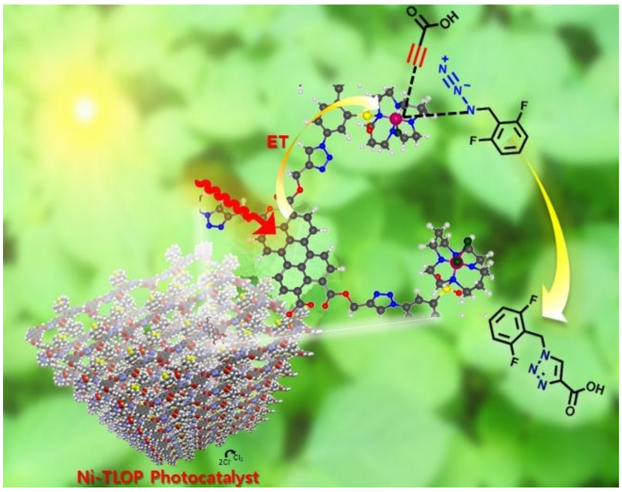
research in an effort to eliminate these shortcomings through various modifications. Additional efforts are still desired to make the azide-alkyne cycloaddition reaction milder and sustainable.

Importance of triazole compounds and its synthetic drawbacks prompted us to design a milder and sustainable approach for the click reaction. In this study, we established greener strategy for solar light assisted selective synthesis of 1,2,3 triazole compounds using postsynthetic modified stilbene-perylene based triazole linked porous organic photocatalyst (TLOP) with Ni(II) as active metal centers (Ni-TLOP) (Scheme I). The synthesized photocatalyst, named as Ni-TLOP, exhibits the extremely high conversion yield of 99.9 % and the superb regioselectivity for the synthesis of 1,5 triazole compounds. Instead of employing the additional reagents and the harsh conditions in synthetic procedure, we adopt the visible-light induced synthesis in co-presence of both Ni-TLOP as photocatalyst and alkyne-azide as reactants, resulting in the formation of regioselective triazole. Furthermore, the Ni-TLOP retains its own catalytic activity for the continuous recycling experiments (5 cycles) with considerable selectivity and stability. We also varify our method on the synthesis of commercial triazole based drugs rufinamide.

Results and discussion

The present work represents the synergistic effect between the visible light active TLOP with Ni(II)Cyclam catalytic sites that can be anticipated for achieving effectual organic transformation to be driven by visible light. In this regard, we choose to construct a TLOP (Figure 1) using simple constituents namely, tetra alkyne substituted perylene and 4,4'-diazidostilbene-2,2'-disulfonic acid disulfonylchloride (L_3) covalently linked through azide-alkyne cycloaddition reaction.



Scheme 1 Graphic presentation of the TLOP photocatalyst mediated synthesis of triazole compounds through azide-alkyne cycloaddition reaction in presence of visible light

The perylenes are well-known active components of photocatalytic systems with high absorption ability and optical tunability on the visible region,[35-37] while the stilbenes being photo-responsive[38] can be anticipated to enrich the system for efficient photocatalysis. The rationale for using stilbene as a building unit is as following: first, the stilbene can induce light assisted interactions within the designed TLOP and second, the sulfochlorinated ($-SO_2Cl$) sites in stilbene could provide the binding sites for the Ni(II) cyclam catalytic centers to the visible light active covalent polymer.[39]

The TLOP was synthesized via cycloaddition reaction of tetra(prop-2-yn-1-yl) perylene-3,4,9,10-tetracarboxylate (L_1) with 4,4'-diazidostilbene-2,2'-disulfonylchloride (L_3) in presence of DIEPA under reflux until complete consumption of L_3. Further, subsequent addition of cyclam and its metalation with $NiCl_2$ lead to the formation of Ni-TLOP as depicted in Figure 1. The as-synthesized TLOP and Ni-TLOP were characterized by the spectroscopic measurement such as FTIR and XPS analysis and the molecular structure of Ni-TLOP was modelled with the molecular mechanics method. Specifically, to extract the structural information of synthesized TLOP, we implemented the molecular mechanical modelling of TLOPs with nine pores using MM2 forcefield.[40] As shown in Figure 2, the optimized structure for the macromolecular units clearly exhibited the tetragonal pores with the diameter of 31.1 Å where the Ni-cyclam covalently linked to the backbone are located. The presences of tetragonal pores in Ni-TLOP is highly linked to the significant Bragg peaks observed in powder X-ray diffraction (PXRD). According to the PXRD patterns for Ni-TLOP shown in Figure 3a, the prominent Bragg peaks were observed for Ni-TLOP with 2θ values at 9.5°, 12.3°, 17.2°, 24.7°, 27.5° and 27.8°. Compared with the PXRD pattern for the neat TLOP, the marginal peak shifts of Bragg patterns were observed for in Ni-TLOP. Nonetheless, judging from the retention of 2θ peaks of TLOP in Ni-TLOP, we noted that the deformation of framework structure was negligible in the metalation process.

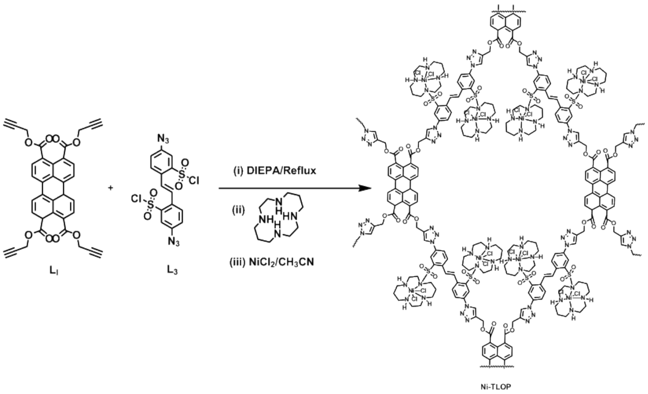


Figure 1: Synthetic approach for synthesis of Ni-TLOP.

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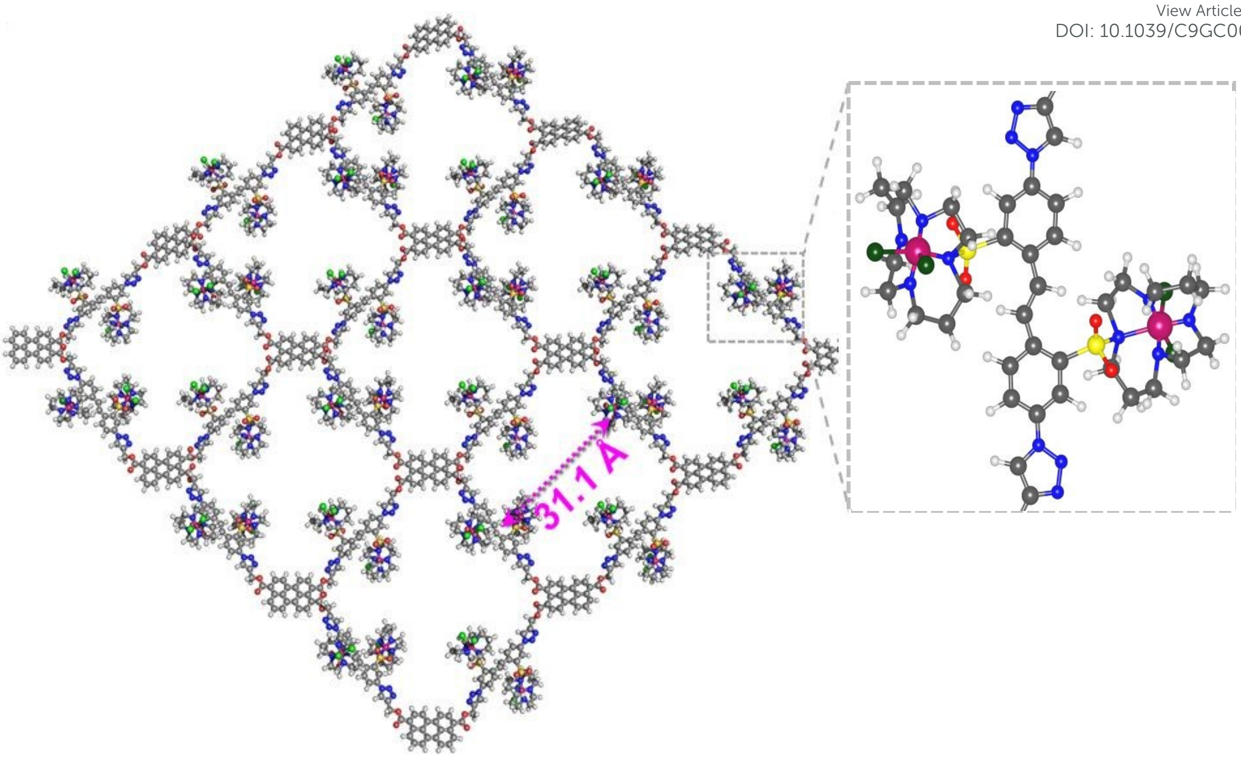

Figure 2: Molecular structure of the Ni(II) cyclam integrated triazole linked organic polymer (Ni-TLOP) optimized by the molecular mechanics calculation. Inset is the magnified view of the Ni-cyclam catalytic center covalently appended to the stilbene backbone.

The FTIR studies were important to confirm the formation of triazole ring in the synthesized 2D framework. Figure 3b displays the FTIR spectra of Ni-TLOP (green line), TLOP (red line) and L_2 (black line) respectively. The formation of triazole ring in the TLOP structure could be confirmed by the disappearance of IR peak around 2100 cm^{-1} corresponding to stretching mode of azide functional group in Ni-TLOP and the concomitant appearance of new stretching bands at 1694 cm^{-1} for the –N=N- and a weaker band at 2962 cm^{-1} for –C=CH stretching.[41] Furthermore, the appearance of new peak for nickel atom in the EDS elemental mapping (Figure 4a-c,) and the XPS data procured for Ni-TLOP conferred the successful metalation of TLOP with $NiCl_2$ to resulting in the formation of Ni-TLOP (Figure 4d). The ICP analysis of Ni-TLOP estimated 52.35% metalation of the polymer (Table S3, ESI). The XPS spectra of Ni-TLOP displayed two peaks for Ni $2p_{3/2}$ and $2p_{1/2}$ at 852.25 eV and 862.45 eV respectively.[42-43] The HRTEM images of Ni-TLOP as shown in figure 4e and 4f exhibited the formation of layered structures, very similar to those for TLOP (Figure S5, ESI) commonly observed in perylene based frameworks.[44] The FESEM images recorded for TLOP and Ni- TLOP were also in agreement with their HRTEM images and showed layered morphology for both TLOP (figure S6, SI) and Ni- TLOP (Figure 4a).

The optical properties were characterized by the diffuse reflectance UV/visible spectra that show a panchromatic absorption in the broad region from near-UV to visible for both TLOP and Ni-TLOP. The Ni-TLOP showed absorption profile with an absorption maxima at 553 nm as shown in figure 5a with an optical band gap of 2.24 eV. The ESR studies were also conducted to investigate the effect of incorporation of nickel in the polymer. Figure 5b shows the ESR spectrum of TLOP (black) and Ni-TLOP (red) where the light harvesting properties of Ni-TLOP was found better than TLOP (figure 5b) which complied to the absorption studies.

After successful incorporation of nickel redox sites into the light harvesting polymer (Ni-TLOP) it was screened for catalysing azide-alkyne cycloaddition reaction under visible light irradiation. Although nickel has been widely used for catalysis of various chemical reactions its research has been elusive in the fields of click chemistry. Hence, we intentionally screened the azide-alkyne cycloaddition reaction using Ni-TLOP as a photocatalyst under visible light irradiation. The Ni-TLOP acting as a photocatalyst showed both high production yield and high regioselectivity. The NMR studies confirmed complete conversion and formation of 1,2,3 triazoles with the high regioselectivity.

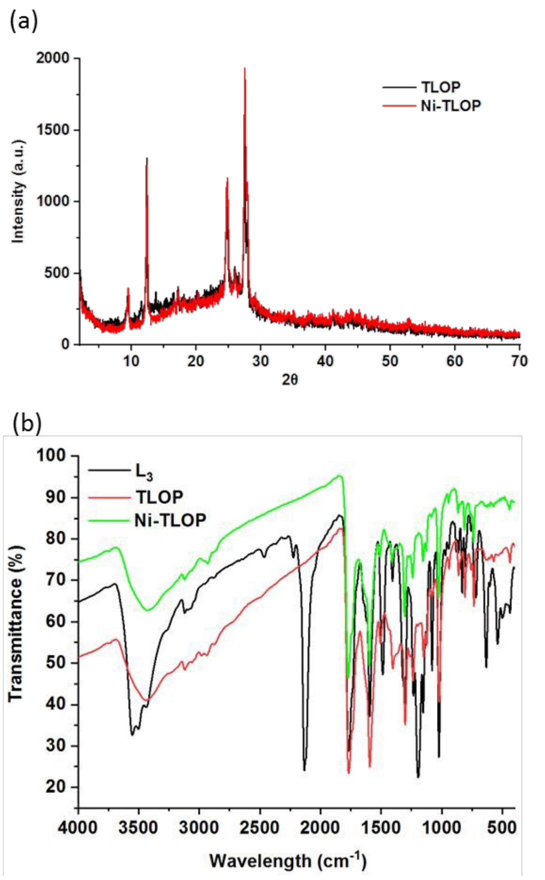

Figure 3 (a) XRD images and (b) FTIR images of Ni-TLOP, TLOP and L_3.

The photocatalysis was conducted in a quartz cuvette with propiolic acid (1a) (1 mmol) and 2,6-difluorobenzylazide (2a) (1 mmol) as reactants, Ni-TLOP as photocatalyst (5 mg), and NaCl (4M, 250 µl) as sacrificial agent under visible light irradiation. The reaction proceeded smoothly with 100 % conversion in 180 mins. The product was abstracted from reaction mixture by addition of chloroform to dissolve the product and followed by centrifugation to separate the photocatalyst. The aliquot was passed through 0.1µm nanopore filter to remove any suspended particles during which immediate crystallization of the product was observed.

The optimization of reaction was a crucial factor to express effective solar click reaction. Hence, the essential components were varied accordingly to get optimum conditions for solar click reaction (ESI, Table S1-2). On account of varying the amount of photocatalyst (ESI, Table S1) and use of co-solvent (ESI, Table S2) the optimum condition obtained were 5 mg of photocatalyst with 250 µl of 4M NaCl in deionized water. Table 1 briefly displays a series of triazole compounds being prepared in good yield and regioselectivity. The substrate scope was investigated varying electronic effect, hindrance, rigidity and flexibility in azides and alkyne substrates. Propiolic acid being one of the major drug component has been screened with aromatic, alkylated, hydroxylated, halogenated, carboxylate and esters functional groups counterparts. In either cases, all the

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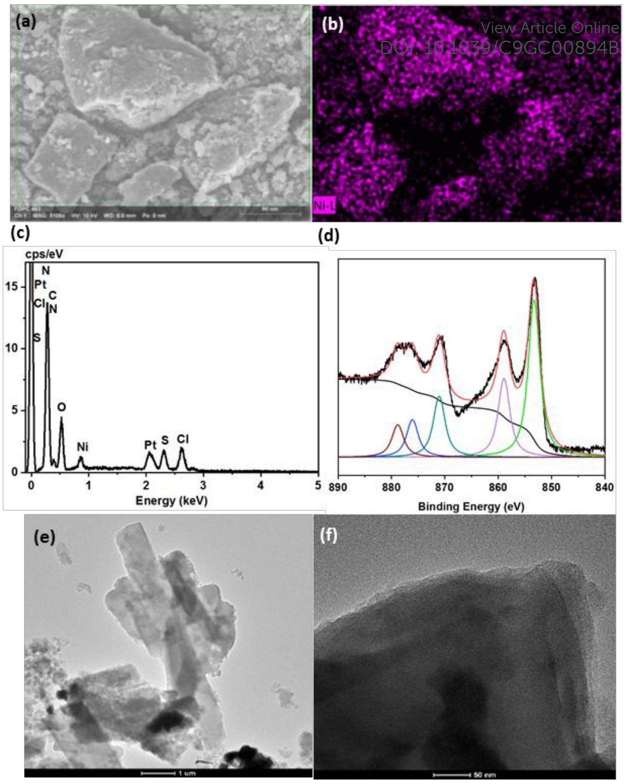

Figure 4 (a) The SEM image and corresponding (b) EDS elemental map for nickel in Ni-TLOP, (c) EDS spectrum showing composition of Ni-TLOP (platinum is observed due to sample prepared on platinum coated copper mount), (d) XPS Ni 2p spectrum for Ni-TLOP, (e) and (f) HRTEM images of Ni-TLOP.

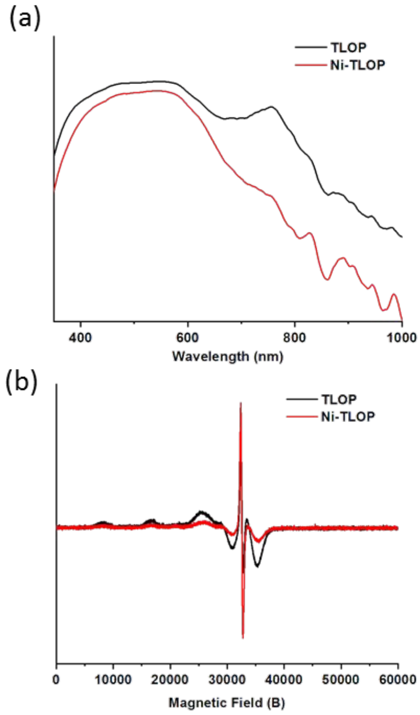

Figure 5 (a) Solid state UV-Visible absorbance and (b) ESR spectra of TLOP and Ni-TLOP.

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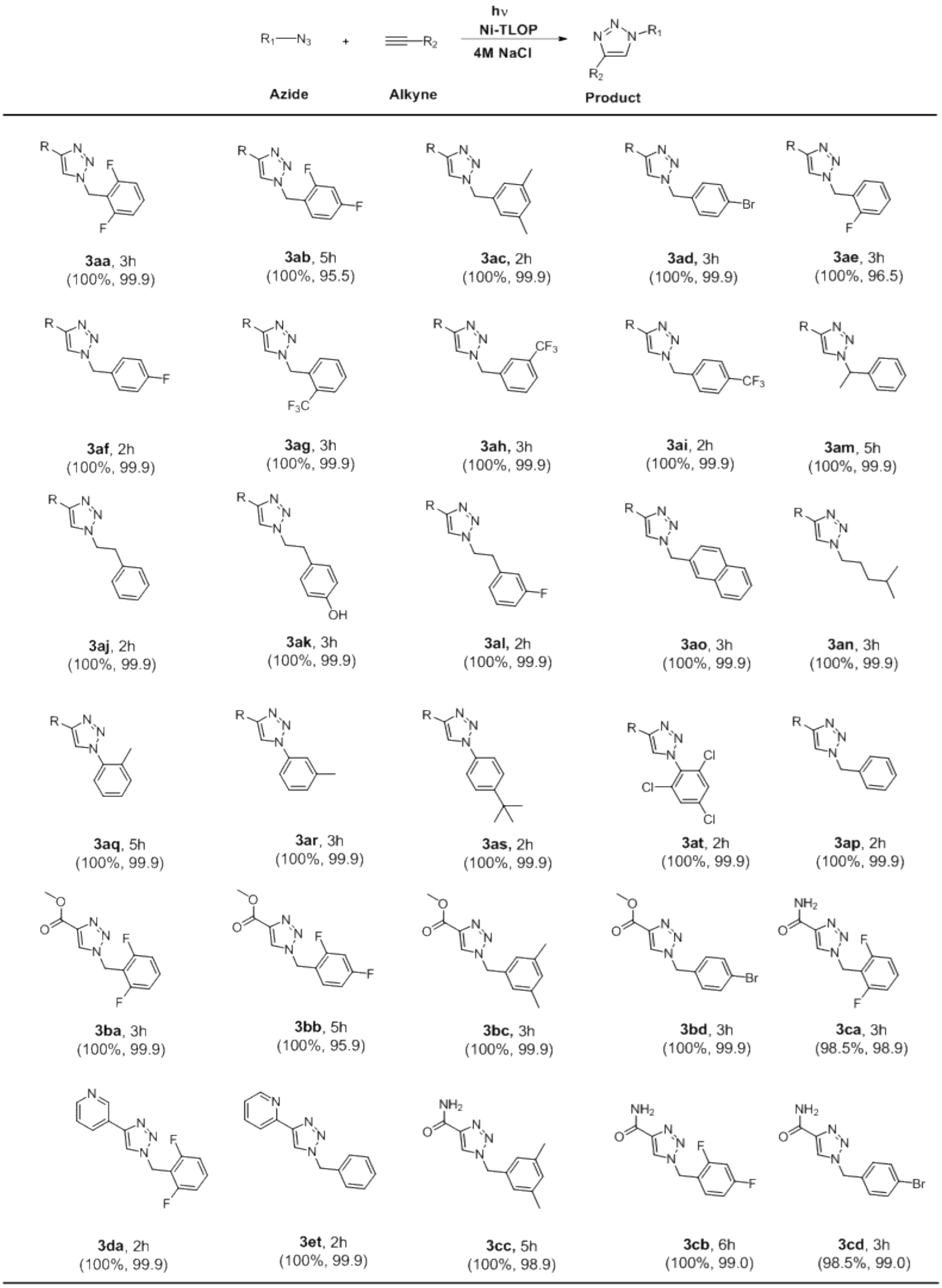
Table 1 Substrate scope for photocatalytic azide-alkyne addition reaction catalysed by Ni-TLOP under visible light irradiation.



3aa, 3h (100%, 99.9)	**3ab**, 5h (100%, 95.5)	**3ac**, 2h (100%, 99.9)	**3ad**, 3h (100%, 99.9)	**3ae**, 3h (100%, 96.5)
3af, 2h (100%, 99.9)	**3ag**, 3h (100%, 99.9)	**3ah**, 3h (100%, 99.9)	**3ai**, 2h (100%, 99.9)	**3am**, 5h (100%, 99.9)
3aj, 2h (100%, 99.9)	**3ak**, 3h (100%, 99.9)	**3al**, 2h (100%, 99.9)	**3ao**, 3h (100%, 99.9)	**3an**, 3h (100%, 99.9)
3aq, 5h (100%, 99.9)	**3ar**, 3h (100%, 99.9)	**3as**, 2h (100%, 99.9)	**3at**, 2h (100%, 99.9)	**3ap**, 2h (100%, 99.9)
3ba, 3h (100%, 99.9)	**3bb**, 5h (100%, 95.9)	**3bc**, 3h (100%, 99.9)	**3bd**, 3h (100%, 99.9)	**3ca**, 3h (98.5%, 98.9)
3da, 2h (100%, 99.9)	**3et**, 2h (100%, 99.9)	**3cc**, 5h (100%, 98.9)	**3cb**, 6h (100%, 99.0)	**3cd**, 3h (98.5%, 99.0)

General reaction condition: Ni-TLOP photocatalyst (5 mg), azide (2a, 1mmol), alkyne (1b, 1 mmol) and NaCl (4M, 250 µl) under visible light irradiation. The conversion and selectivity are stated within brackets respectively. 'R' is denoted for carboxylic group

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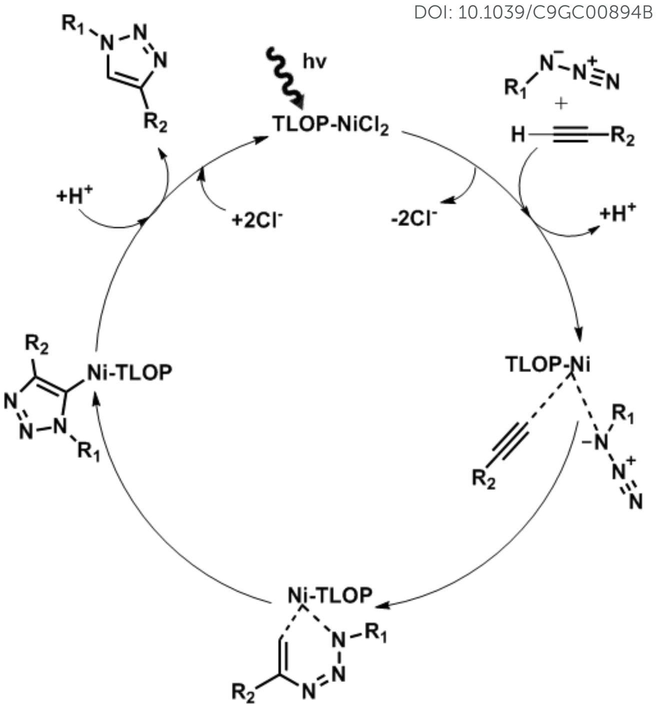
Table 2. Control experiments for Ni-TLOP catalyzed azide-alkyne addition:

Entry	Photocatalyst	Visible light	Conversion(%)[a]
1.	Ni-TLOP	On	100
2.	-	On	-[c]
3.	Ni-TLOP	Off	-[b,c]
4.	TLOP	On	-[c]
5.	Ni-Cyclam	On	25[b,c]
6.	Ni-Cyclam	Off	-[b,c]
7.	$NiCl_2$	On	-[b,c]
8.	$NiCl_2$	Off	-[b,c]

General reaction condition: photocatalyst 5mg, azide (2a, 1mmol) and alkyne (1 b, 1 mmol), 250 µL NaCl (4M in deionized water), under 6h of visible light irradiation (a) Conversion by ^1H NMR analysis. (b) The reaction was run for 24h. (c) No conversion detected.

substrates showed excellent selectivity, conversion and regioselectivity. The conversion, purity and regioselectivity of the products were analysed through ^1H, ^{13}C and ^{19}F NMR (figure S33 – S87, ESI) and X-ray single crystal crystallographic data was also obtained for 3bd. (ESI, Figure S12, table S4, S5).

The mechanistic studies required some essential control experiments to be conducted before it expression. Hence, the control experiments were conducted and the results were summarized in Table 2. The reactants 2,6-difluorobenzyl azide (2a) and propiolic acid (1a) were selected as a model reaction for the systematic assessment of azide-alkyne addition reaction in presence of photocatalyst. The formation of triazole (3a) was achieved in 100 % conversion and 99.9% regioselectivity using Ni-TLOP as the photocatalyst and NaCl (4M) as the sacrificial agent under visible light irradiation for 3 h (Table 2, entry no 1). However, in absence of Ni-TLOP photocatalyst no product formation was observed under similar reaction conditions. (Table 2, entry no 2). When the same reaction was carried out under similar reaction conditions but without visible light illumination no conversion was realized (Table 2, entry no 3). This indicated that the contribution of visible light is essential for the effective photocatalysis. The formation of triazole was also not observed when TLOP was used as photocatalyst (Table 2, entry no 4) under similar reaction conditions. Similar trend was obtained for Ni-Cyclam where the conversion reached 25% (Table 2, entry no 5) in presence of light and no conversion was observed in absence of light (Table 2, entry no 6). $NiCl_2$ on the other hand did not catalysed the azide-alkyne cycloaddition reaction under similar reaction conditions in presence (Table 2, entry no 7) and/or absence of light (Table 2, entry no 8).



Scheme 2: Proposed mechanism for Ni-TLOP catalyzed azide-alkyne cycloaddition reaction in presence of visible light.

The key findings from the control experiments indicated that excellent photocatalytic activity originated from the Ni(II) centers in TLOP photocatalyst by visible light which offers a sustainable approach to this catalytic transformation. The absence of either visible light, and/or metallized photocatalyst (Ni-TLOP) did not led to formation of triazole product. Also, the use of green solvent water as a reaction media and NaCl as sacrificial agent highlight the greener catalytic approach towards visible light mediated synthesis of triazole products. Conclusively from the above key findings, we tentatively suggest the Ni-TLOP mediated solar click reaction as described in Scheme 2.

The Photophysical properties of Ni-TLOP confers its light harvesting property in the visible region (figure 5a). The DRS UV-Visible absorption profile of Ni-TLOP displayed an optical band gap of 2.24 eV enabling it to efficiently harvest photons upon visible light irradiation. The photoexcited electrons thus generated reduce the nickel (II) with expulsion of chloride anions which now readily forms π-complex with alkynyl species.[45, 46] The initial π-complex formed between the Ni center and alkyne molecules results in lowering of the pKa value of the terminal acetylene facilitating proton abstraction and formation of terminal acetylene complex.[26d] The formation of nickel-acetylidine complex followed by addition of azide molecule leads to the formation of an intermediate metallacycle complex. Which upon subsequent formation of triazole ring followed by protonation results in elimination of the product from the catalytic cycle. The chloride ions eliminated are recycled back into the catalytic cycle regenerating Ni(II) for continuous photocatalysis.[45] The addition of NaCl (4M) as sacrificial agent helps in scavenging the holes generated by photoexcitation. The chloride ions thus gets oxidised to chlorine (Cl_2) which in presence of water disproportionate into HClO and HCl.[47] The HCl could also contribute in regeneration of Ni(II)centers by providing chloride ions essentially required for photocatalysis.[45]

Recyclability is a necessity for heterocyclic catalyst and an essential need for sustainable photocatalysis. The recyclability of Ni-TLOP was also tested up to five cycles (Figure S1, SI). The photocatalyst was readily recovered from the reaction mixture after centrifugation and washing with acetone and chloroform, followed by drying at 100˚ C in vacuum before next catalytic run under identical conditions. The yield was up to 90% for five consecutive recycling experiments (figure S1, ESI) with negligible leaching of Ni in the triazole product. The first cycle of catalysis showed the presence of 10 ppm Ni which was decreased further to less than 7 ppm in the recycling experiments (table S3, ESI). The robustness of the photocatalyst for confirmed via FTIR (figure S7, ESI), FESEM (figure S8, ESI), HRTEM (figure S9, ESI), PXRD analysis (figure S10, ESI) and XPS (figure S11, ESI). The stability and robustness of the Ni-TLOP makes it an ideal candidate for immobilization of metal centers and their use in light assisted chemical transformations.

We employed our optimized solar-click reaction process for the synthesis of one of the most selling triazole based commercial drugs rufinamide to one gram scale, an antiepileptic drug to treat Lennox–Gastaut syndrome, in combination with other medications (entry 9 in Table 1, page S7 and figure S1, ESI). Easy and feasible production of rufinamide has been continuously researched from time to time.[48,49] However, the process suffers from either multistep synthesis, low regioselectivity, low conversion, harsh reaction conditions, prolonged reaction time and possibility of metal contamination in the final product. [33] One-pot reaction assisted by solar light and our photocatalyst Ni-TLOP resulted in quantitative and regioselective synthesis of rufinamide.

Conclusions

We newly designed a highly active heterogeneous photocatalyst immobilising Ni(II) on covalent organic polymer via postsynthetic modification. The new photocatalyst successfully employed to establish a greener and sustainable approach for functional group tolerant regioselective photo-synthesis of triazole based compounds in base free conditions. The catalyst was readily recovered after the completion of the reaction and was able to be recycled for at least five cycles without deterioration of the product yield. We also verified that no immobilised metal was leaching from the photocatalyst even on recycling the photocatalyst. The air and moisture stability of the photocatalyst making it applicable for broad range of substrates. The method has also been successfully tested for greener and milder synthesis of triazole functionalised antiepileptic drug rufinamide. The visible light irradiation activates the photocatalyst by reversibly breaking the metal-chloride bond and continuously producing the active metal centers. However, additional mechanistic studies are required for full establishment of our proposed mechanism. Development of efficient, robust and visible light active photocatalyst by immobilisation of metal opens a new avenue for superb regioselective and sustainable photosynthesis of important organic compounds.

Experimental

Materials

All the reagents utilized in synthesis were purchased from commercial suppliers, unless or otherwise stated. Please refer to section 2 of the supplementary information for safe handling of azides.

Instruments and Measurements:

^1H and ^{13}C spectra were recorded on a Bruker AVANCE II+ 500 MHz spectrometer with tetramethylsilane (TMS; δ = 0) as internal standard. Solid state UV-Visible spectra were recorded on Shimadzu UV-1800 spectrophotometer. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Bruker ALPHA-T FT-IR spectrometer. The test specimens were prepared by the KBr-disk method. Wide-angle X-ray diffraction (XRD) analyses were carried out by using an X-ray diffractometer (D/MAX-2200, Rigaku Denki). The X-ray diffraction patterns were recorded in the range of $2\Theta = 2–70˚$ with Cu K_α radiation (λ= 1.5406 nm) at 40 keV and 100 mA. XPS spectra were recorded on Axis Nova photoelectron spectrometer (KRATOS). The samples for EDS and FESEM analysis were prepared on Pt coated Cu mount. The Energy Dispersive X-ray studies (EDS) were carried out on Bruker Quantax 200 Energy Dispersive X-ray Spectrometer equipped with Si Drift Detector (SDD) [Energy Resolution : <123eV, Peak shift (5~300 kcps) : < 5eV, and Detection: Be (z=4) - Am (z=95)]. The FESEM images were procured by Carl Zeiss ΣIGMA HD FESEM instrument at 10 keV. The Xenon lamp (Newport 66921) with a 420 nm cut-off-filter as light source (100 mW/cm2) was used for photocatalytic reactions. The ICP analysis for nickel was carried out using thermos scientific iCAP 7400 duo inductively coupled plasma atomic emission spectrometer (ICP-AES).

Synthesis of (E)-1,2-bis(2-((1,4,8,11-tetraazacyclotetradecan-1-yl)sulfonyl)-4-azidophenyl)ethene (TLOP):

L_1 (1g, 1 mmol) was dissolved in dry DMF (250mL) with constant stirring under argon. DIEPA (0.6 mL, 2mmol) was added to the reaction mixture followed by L_3 (1.57 g, 2 mmol). The reaction mixture was refluxed until complete consumption of L_3. After the completion of the reaction, cyclam (0.7 g, 10mmol) was added to the reaction mixture. The reaction was refluxed further for 24 h. The crude product was precipitated in water (50 mL) and the solid obtained was filtered out using a G4 glass filter. The solid obtained was washed with $CHCl_3$ (2 x 25 mL), MeOH (2 x 25 mL), acetone (2 x 25 mL) and water (2 x 25 mL). The solid was again suspended in MeOH (150 ml) and stirred overnight.

The precipitate was then filtered and vacuum dried overnight to get TLOP in an isolated yield of 90%.

Synthesis of [(E)-1,2-bis(2-((1,4,8,11-tetraazacyclotetradecan-1-yl)sulfonyl)-4-azidophenyl)ethane Ni(II)Cl$_2$] (Ni-TLOP):
TLOP 1(0.50g) was suspended in dry CH_3CN (50mL) followed by addition of $NiCl_2$ (0.54g) and the reaction mixture was stirred for overnight. After metalation the colour of the suspension was darken and the precipitated product was filtered out using a G4 glass filter. The solid obtained was washed with MeOH (2 x10 mL) and CH_3CN (50mL) followed by vacuum drying overnight to get 0.47g of Ni-TLOP photocatalyst.

General procedure for photocatalytic alkyne-azide click reaction:
In a cuvette, photocatalyst (5 mg) and alkyne derivative (1 mmol) were stirred at room temperature for 5 mins followed by addition of azido derivative (1 mmol) and NaCl (4M, 250µL). The reaction mixture was vigorously stirred under visible light irradiation until completion of reaction. The mixture of ethanol/chloroform (5 mL) was added to isolate the product and photocatalyst by simple filtration followed by drying. The photocatalyst recovered via filtration was successively washed with $CHCl_3$, acetone and water and dried under vacuum before reusing. The detail characterization of the triazole derivative and the recovered photocatalyst are given in the supplementary information file.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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