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Received 6th June 2021, Accepted 10th August 2021 DOI: 10.1039/d1gc02002a rsc.li/greenchem Dipolar HCP materials as alternatives to DMF solvent for azide-based synthesis[†]

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Hypercrosslinked polymers HCP-DMF and HCP-DMF-SO₃H containing abundant and flexible DMF moieties were designed and synthesized. Benefitting from the solvation microenvironment provided by the pseudo-DMF moities, the polar HCPs manifested outstanding performances in the conversions of NaN₃ to benzylic azides and 1,2,3-triazoles in EtOH (95%), respectively, avoiding the use of risky DMF and improving the separation processes of the products.

The activities and selectivity of organic conversions are significantly influenced by the choice of reaction media. Traditional dipolar aprotic solvents (DMSO, DMF, DMAc, NMP, etc.) play an important role in rendering outperformance for a wide range of reactions including the S_N2 reaction,¹ Pd-catalyzed coupling reactions,²⁻⁴ conversion of azides⁵⁻⁸ to biomass valorization.9 However, wastewater and high energy input accompany the product separation and solvent recycling due to the utilization of such a class of high boiling solvents.¹⁰ When it comes to DMF, there are more problems, resulting from more CMR issues (carcinogenic, mutagenic, or reprotoxic) as compared to DMSO. It has also been reported that DMF has more potential safety risks in chemical processes because it is incompatible with a large variety of substances, producing dimethylamine as well as gaseous products CO₂, CO and H₂, leading to many incidents over the years.^{11,12} Being aware of these hazards, it is appealing to the scientific community to identify and develop safer and greener alternatives to DMF.

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Despite the fact that biobased solvents γ -valerolactone (GVL), dihydrolevoglucosenone (CyreneTM) and dimethyl isosorbide (DMI) have been proved to have the ability to replace DMF in many organic reactions,^{13–16} their high boiling points and easy miscibility with water result in wastewater discharge and energy-intensive processes for recycling. In addition, solid-phase peptide synthesis (SPPS) also suffers from similar troubles when some alternatives to DMF are used such as *N*-butylpyrrolidinone (NBP) and binary solvents DMSO/DOL (1,3-dioxolane) and DMSO/2-Me-THF.^{17–19}

Creating a local solvation environment for the active sites in heterogeneous catalysts provides potential and opportunities to conduct some organic reactions in low boiling solvents, thus allowing us to avoid the use of conventional dipolar aprotic solvents. For instance, porous polymer solvents (PPSs) with a DMSO moiety and acid COFs incorporating flexible PVP in channels promote the dehydration of fructose to HMF efficiently in THF rather than in DMSO, which is always required in common processes.²⁰⁻²² However, the complicated design of catalysts and the use of hazardous solvents, like THF, reflect their limitations in multitudinous organic reactions to realize green prospects. Hypercrosslinked polymers (HCPs) have been widely used in many applications, such as gas separation and conversion,^{23,24} catalysis,²⁵ and energy storage,²⁶ because of their low cost and ease of preparation from various organic monomers.²⁷ Benefiting from permanent porosity, high stability and modifiable functionality,28 HCPs-based catalysts exhibit multipurpose functions in organic synthesis. Indeed, HCP materials enabled us to easily introduce diverse active sites and local microenvironments in the catalysts, facilitating the model transformations including acid-base tandem reactions²⁹ and a variety of name coupling reactions.³⁰ The high propensity of HCP materials for solvent uptake also ensured they were suitable precursors to design heterogeneous catalysts equipped with a solvation microenvironment.³¹

The synthesis and conversion of azides is a common route to support triazoles and tetrazoles which are two significant scaffolds in numerous bioactive molecules and functional

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materials.^{8,32,33} NaN₃ is the most commonly used starting material to obtain organic azides and further construct triazoles and tetrazoles compounds.^{34,35} However, in the synthesis of these compounds, the habitual use of DMF as a reaction medium for these processes results in a series of issues as previously mentioned.^{5,6,36} Therefore, more effort should be made to minimize and avoid the use of DMF in a much greener strategy for the transformation of azides.

Based on the readily designable and swelling properties of HCP materials, in this work, we tried to design dipolar HCPs with a flexible DMF moiety as solid PPSs with an expectation to create a dipolar microenvironment for promoting reactions. Ideally, with the aid of this special HCP material, greener solvents can be used as alternatives to DMF in the conversion of NaN₃ to benzylic azides and triazoles.

Polar HCP materials with a DMF moiety were prepared according to the route shown in Scheme 1. N-Methyl-N-(3-phenylpropyl)formamide M1 was used as the monomer to obtain HCP-DMF via a hypercrosslinking reaction. The following sulfonation reaction using acetyl sulfate can convert HCP-DMF to HCP-DMF-SO₃H, which was expected to act as an acid catalyst with a dipolar microenvironment for active sites. The long side chain in the aromatic ring of monomer M1 ensures HCP-DMF has flexible DMF moieties. In HCP-DMF-SO₃H, the accessibility of the DMF moieties to the active acid sites is also expected, maximizing the positive effect of the local environment on the catalytic reaction. For comparison, the two materials of HCP-Ben and HCP-DMF-Ben were also prepared in order for us to investigate the influence of the DMF moieties content. The first one was fabricated using benzene M2 as the monomer and the second one was prepared by using a mixture of M1 and M2 as the monomers.

The DMF moieties in HCP-DMF and HCP-DMF-SO₃H were demonstrated by the FT-IR spectra as described in Fig. 1(a). The conspicuous peaks at about 1662 cm⁻¹ both in HCP-DMF and HCP-DMF-SO₃H were attributed to the stretch vibration of the C=O bond of DMF moieties, which correspond to that of **M1**, obviously suggesting the successful synthesis of HCP-DMF and the preservation of DMF moieties even after sulfonation to obtain HCP-DMF-SO₃H. Compared with HCP-DMF, the emerging two peaks at 1220 cm⁻¹ and 1188 cm⁻¹ in HCP-DMF-SO₃H were related to the stretching vibration of the S=O bond of aromatic sulfonic acid, indicating the successful



Fig. 1 (a) The FT-IR spectra of HCP-DMF and HCP-DMF-SO₃H; (b) fluorescence emission spectra of Nile red adsorbed in different HCP materials; (c) TGA curves of HCP-DMF and HCP-DMF-SO₃H; (d) solid-state ¹³C NMR; (e) C 1s and (f) N 1s XPS spectra; and SEM images of (g1) HCP-DMF, (g2) HCP-DMF-Ben, (g3) and HCP-Ben.

acidification.³⁷ The existence of -SO₃H on the HCP-DMF-SO₃H is also indicated by a weak peak at 1035 cm⁻¹ due to the C(aromatic)-S stretching vibration.³⁸ Nile red (NR) has been widely used as a probe to determine the polarity of microenvironments in various heterogeneous materials via its fluorescence spectra.³⁹⁻⁴¹ The fluorescence emission spectra of NR adsorbed in different HCP materials were used to estimate the polarity of prepared HCPs, as shown in Fig. 1(c). Upon photoexcitation at 420 nm, the fluorescence intensity of NR adsorbed in HCP-Ben, HCP-DFM-Ben and HCP-DMF became obviously weaker and almost disappeared with the increasing content of monomer M1; a slight red shift from 636 nm to 647 nm in the fluorescence maximum of the NR was also noticed. The weakened intensity and red shift can be ascribed to the stabilized twisted intramolecular charge transfer state (TICT) of NR by a polar environment.⁴² Such a fluorescence behavior of the dye demonstrated that the polarity of HCP-Ben, HCP-DFM-Ben and HCP-DMF was enhanced gradually because of the decoration of the DMF moieties. The thermal stability of both HCP-DMF and HCP-DMF-SO₃H were inspected by



Scheme 1 A schematic illustration of polar HCPs in terms of their structure and preparation.

thermogravimetric analysis (TGA), as shown in Fig. 1(c). It was observed from the TGA curves that the weight of two kinds of HCP materials was maintained until the temperature was elevated to about 140 °C and the initial decomposition temperature was nearly 200 °C. The TGA results implied that the prepared materials have a good thermostability to be used under mild conditions. Solid-state ¹³C NMR and XPS were employed to investigate the situation of the DMF-like moieties and the sulfonic moieties, the spectra are shown in Fig. 1d-1f. It is observed from Fig. 1d that the carbon peak at 164 ppm ascribed to -N-CHO emerged and increased with the addition of monomer M1. Besides, the unaltered chemical shift of C in HCP-DMF-SO₃H and HCP-DMF-Ben-SO₃H indicated that sulfonation did not have an impact on the DMF-like moieties, which is consistent with the FT-IR spectra results. Such an interpretation is also reinforced by the N 1s XPS spectra (Fig. 1(e)), in which the shape and binding energy of N 1s remain after the sulfonation of HCP-DMF to HCP-DMF-SO₃H. The C 1s peak could be resolved into main three peaks as shown in Fig. 1(f), in which the binding energy of C=O (287.3 eV) in HCP-DMF-SO₃H and HCP-DMF-Ben-SO₃H shows no obvious change. All the results disclosed by the ¹³C NMR and XPS spectra suggest that although DMF-like moieties were successfully introduced and remained after sulfonation of HCP-DMF, there is almost no interaction between the DMFlike moieties and -SO3H at the site-isolation state in HCP-DMF-SO₃H.

The scanning electron microscopy (SEM) images disclosed clearly that the morphologies of the three classes of HCPs changed from the dense and blocky texture of HCP-DMF (Fig. 1g1) to the loose and porous structure of HCP-Ben (Fig. 1g3) with the decrease of monomer **M1** in the HCPs, while both a compact and lax structure was presented in HCP-DMF-Ben (Fig. 1g2). The $-SO_3H$ concentration of HCP-DMF-SO₃H, HCP-DMF-Ben-SO₃H and HCP-Ben-SO₃H was 1.2×10^{-3} , 1.2×10^{-3} and 1.0×10^{-3} mmol mg⁻¹, respectively, which were calculated according to the S content (see ESI[†]) determined by elemental analysis (EA).

We also investigated the specific surface S_{BET} and swelling property of three kinds of HCPs and the results are tabulated in Table 1. It was noticed that the S_{BET} of the HCP materials dramatically decreased from 1266.7 m² g⁻¹ of HCP-Ben to 0.9 m² g⁻¹ of HCP-DMF with the increase of **M1** content. After sulfonation of HCP-DMF, the S_{BET} of HCP-DMF-SO₃H is kept at 1.1 m² g⁻¹. There are almost no pores in HCP-DMF. The changed S_{BET} of different HCP materials were consistent with the SEM images in Fig. 1. The swelling degree Q of three kinds of HCP materials in EtOH (95%) was determined as shown in Table 1. HCP-Ben has the largest Q (603%) benefitting from its

| Table 1 Properties of different HCP materials | | | | | | |
|--|---------------|-------------|-----------|--|--|--|
| Material | HCP-Ben | HCP-DMF-Ben | HCP-DMF | | | |
| $\frac{S_{\text{BET}} \left(\text{m}^2 \text{g}^{-1}\right)}{Q \left(\%\right)}$ | 1266.7 603 | 50.6 150 | 0.9 67 | | | |

highest S_{BET} . Reasonably, the swelling degree of HCP-DMF-Ben and HCP-DMF sharply reduced to 150% and 67%, respectively. In fact, the low weight increase of HCP-DMF suggests that HCP-DMF has hardly any swelling ability in EtOH (95%) subjected to its low S_{BET} . Because of the deficient swelling degree of HCP-DMF, the predominant contribution of the DMF moieties to the polar solvation microenvironment could be expected, thus facilitating the maximization of the solvent effect of the supporting materials.

Nucleophilic substitution of NaN3 to benzyl bromides is a usual pathway to synthesize benzylic azides as an important intermediate to triazoles, it is always performed in DMSO or DMF without the addition of a catalyst at high temperature for a long time.^{5,6,43,44} With the polar HCPs in hand, we then examined their function in the replacement of DMF by using the reaction of NaN₃ to p-methylbenzyl bromide 1a to synthesize p-(azidomethyl)toluene 2a. As shown in Table 2, in the presence of HCP-DMF, various green solvents, including anisole, isopropyl acetate (¹PrOAc), 2-methyltetrahydrofuran (2-MeTHF) and ethanol (EtOH), were screened for the S_N2 reaction at ambient temperature firstly (entries 1-5). It was found that this reaction cannot proceed in anisole (entry 1) and only trace product was observed by TLC with a much lower conversion of starting material in ⁱPrOAc and 2-MeTHF (entries 2 and 3). In anhydrous EtOH, the yield of 2a reached 27%, which is promising and deserves further optimization. quite Considering the low solubility of NaN₃ in anhydrous ethanol, EtOH (95%) was used then as reaction medium. To our delight, an excellent yield of 2a (92%) was obtained in the presence of HCP-DMF (entry 5). However, only 69% 2a was separated in EtOH (95%) without adding the HCP-DMF component (entry 6). When HCP-DMF-Ben and HCP-Ben were added into the reaction system, the yields of the target compound gradually reduced from 78% to 67% (entries 7 and 8) mainly caused by the fading dipolarity of the corresponding HCP materials (Fig. 1(b)). The comparable yields of 2a in entry 8 and entry 6 indicated that HCP-Ben hardly has any influence on the reaction process. All the above results reflected that the introduc-

| Br | | Additive (30 mg) | N ₃ | |
|-------|----------------------|--------------------|----------------|--|
| | + NaN ₃ - | Solvent, RT, 1.5 h | | |
| 1a | | | 2a | |
| Entry | Solvent | Catalyst | Yield (%) | |
| 1 | Anisole | HCP-DMF | NR | |
| 2 | ⁱ PrOAc | HCP-DMF | Trace | |
| 3 | 2-MeTHF | HCP-DMF | Trace | |
| 4 | EtOH | HCP-DMF | 27 | |
| 5 | EtOH (95%) | HCP-DMF | 92 | |
| 6 | EtOH (95%) | None | 69 | |
| 7 | EtOH (95%) | HCP-DMF-Ben | 78 | |
| 8 | EtOH (95%) | HCP-Ben | 67 | |

Table 2 The optimization of benzylic azides synthesis from ${\sf NaN_3}$ and benzyl bromide a

^a 1a, 0.3 mmol, NaN₃, 0.35 mmol, 1.5 h, isolated yields.

tion of DMF moieties greatly accelerated the nucleophilic substitution of NaN_3 to **1a**. The highest yield obtained by HCP-DMF also highlighted that the polarity of the material is pivotal even though it has poor pores. Thus, benzyl azide and the reaction conditions as listed in entry 5 were viewed as worthy of optimization for further study. Importantly, the product can be isolated conveniently by simple filtration, drying and concentration thanks to the complete conversion of benzyl bromide and excellent selectivity to product.

The substrate scope of substituted benzyl bromides was subsequently investigated under standard conditions, and the results are given in Scheme 2. Diverse benzyl bromides bearing diverse substituents were compatible with the standard conditions. Various substituents in the aryl ring of 1 are tolerable, and the desired products 2b-2r can be obtained in yields ranging from 88–95% without electronic and steric effects. Compared to the above results, only inferior yields (2band 2f) were reached without the addition of HCP-DMF. It was noted that 93% 2q was isolated when 1,2-dibenzyl bromide and 2.3 equivalents of NaN₃ were used as the starting materials. A substrate containing *N*-heterocyclic ring 1r also afforded a 95% yield of 2r (Scheme 2).

Given the outstanding performance of HCP-DMF in EtOH (95%), we would like to use its corresponding acidified material HCP-DMF-SO₃H as a catalyst to promote the 1,3dipolar cycloaddition of nitroolefin to NaN₃ to synthesize 1,2,3-triazole which is a significant scaffold in widespread drug analogs with bioactivities such as antimicrobial, antiviral and antitumor effects.³³ There are similar issues in that the process is usually carried out in DMF or DMSO solvents and thus is associated with environmental and health concerns.^{7,45-47} The upgraded catalyst HCP-DMF-SO₃H with a pseudo-DMF microenvironment for acid sites gives us an opportunity to replace DMF in this reaction. Some green solvents were investigated again in the presence of 10 mg HCP-DMF-SO₃H and no conversion of 3a was observed in anisole, ⁱPrOAc or 2-MeTHF at 60 °C (Table 3, entries 1-3). What is promising is that a 24% yield of 4a was separated in EtOH (entry 4), which improved to 46% when EtOH (95%) was used (entry 5). The lower yields in entries 6 and 7 were probably caused by the decrease of M1 content in the catalyst poly-



Scheme 2 The substrate scope of benzyl bromides to benzyl azides. ^a0.7 mmol NaN₃ was added, the yields in parentheses were obtained without the addition of HCP-DMF.

Table 3 The assembly of 1,2,3-triazoles from nitroolefin with NaN_3^a

| | NO ₂ + NaN | Catalyst (10 mg) | N=N NH |
|------------|--------------------------|-------------------------------|-----------|
| MeO | 3a | Solvent, 60 °C, 2 h MeO | 4a |
| Entry | Solvent | Catalyst | Yield (%) |
| 1 | Anisole | HCP-DMF-SO ₃ H | NR |
| 2 | ⁱ PrOAc | HCP-DMF-SO ₃ H | NR |
| 3 | 2-MeTHF | HCP-DMF-SO ₃ H | NR |
| 4 | EtOH | HCP-DMF-SO ₃ H | 24 |
| 5 | EtOH (95%) | HCP-DMF-SO ₃ H | 46 |
| 6 | EtOH (95%) | HCP-Ben/DMF-SO ₃ H | 32 |
| 7 | EtOH (95%) | HCP-Ben-SO ₃ H | 21 |
| 8 | EtOH (95%) | Amberlyst 15 | 17 |
| 9^b | EtOH (95%) | HCP-DMF-SO ₃ H | 79 |
| $10^{b,c}$ | EtOH (95%) | HCP-DMF-SO ₃ H | 92 |

 a 3a, 0.3 mmol, NaN3: 0.35 mmol, catalyst: 10 mg, isolated yields. b 20 mg catalyst. c 4 h.

meric matrix. However, with the commercial bead Amberlyst 15, **4a** was obtained in 17% yield (entry 8), which was lower than that of HCP-Ben-SO₃H (21%). It is inferred that diffusion limitation and less swelling of the bead Amberlyst 15 caused its lower activity compared to powder HCP-Ben-SO₃H. Finally, the yield of **4a** was enhanced to 92% by increasing the dosage of HCP-DMF-SO₃H to 20 mg and lengthening the reaction time to 4 h (entries 9 and 10). The encouraging results proved that the combination of HCP-DMF-SO₃H with EtOH (95%) indeed gave a suitable alternative to replace DMF in the synthesis of 1,2,3-triazole from nitroolefin and NaN₃.

After the optimized conditions were established based on entry 10 in Table 3, we then investigated the reaction scope in terms of nitroolefins (Scheme 3). Nitroolefins bearing electrondonating or -withdrawing groups on aryl rings gave the corresponding products in high to excellent yields (82%–94%)



Scheme 3 Nitroolefin substrates to synthesize 1,2,3-triazoles. ^a10 h.

within 4–6 h, suggesting that this polar catalyst manifested great activity and selectivity toward diverse nitroolefins in EtOH (95%) and the electronic nature of nitroolefins has only a little influence on the 1,3-dipolar cycloaddition. In addition, the reaction with a heterocyclic substituted nitroolefin, **31**, also proceeded smoothly, giving the expected product **41** in 85% yield. However, (*E*)-3-(2-nitrovinyl)-indole **3m** was reluctant to participate in the reaction and the target product **4m** was only obtained in 58%, probably resulting from the alkalinity of **3m**. The low activity of **3m** was also observed in other reports so harsh conditions were required to improve the yield of **4m**.⁷

It is also possible to combine the conversion of benzyl bromide to benzyl azide and the cycloaddition with nitroolefins to 1,4-disubstituted-1,2,3-triazoles together to establish a tandem process. Out of this consideration, a three-component reaction of **1a**, **3a** and NaN₃ was investigated by using the DMF-containing HCPs as promoting materials. As shown in Scheme 4, **5a** was obtained in 58% yield in the presence of HCP-DMF-SO₃H. When Amberlyst 15 was used as the catalyst, the yield only reached 33%, indicating again the promoting effect of the DMF moiety on the HCP-based catalyst (Scheme 4).

The reaction kinetics of the 1,3-dipolar cycloaddition of nitroolefin to NaN3 further confirmed that the dipolar HCP-DMF-SO₃H catalyst was indeed beneficial for the synthesis of 4a (Fig. 2a). It was noticed that the reaction rate of HCP-Ben-SO₃H was obviously faster than that of HCP-DMF-SO₃H at the initial stage before 2 h mainly because of the large S_{BET} of HCP-Ben-SO₃H providing more active sites. However, the yield of 4a in HCP-Ben-SO₃H was distinctly restrained after 2 hours resulting from the formation of by-products. By contrast, the reaction rate of HCP-DMF-SO₃H remained constant until the substrate was gradually consumed due to its solvation to NaN₃ and the higher selectivity to target product 4a.

The recycling of these two HCP materials was also investigated. HCP-DMF can be efficiently recovered and reused in the model reaction. However, for the recycling of HCP-DMF-SO₃H, we have to consider the possible damage of its activity because H^+ might be exchanged by the Na⁺ of the generated byproduct, a sodium salt, in the cycloaddition. The reuse performance of HCP-DMF-SO₃H was investigated carefully in the reaction of β -nitrostyrene and NaN₃ under standard conditions. Interestingly, the polar catalysts remained highly active even after 7 successive recycles, supporting excellent yields of products above 84% without a dramatic yield decrease compared







Fig. 2 (a) Reaction kinetics for the synthesis of 4a from 3a and NaN₃. (b) Recycle experiment of HCP-DMF-SO₃H in the 1,3-dipolar cycloaddition in EtOH (95%).

to the first run (92%) (Fig. 2). The maintained activity of HCP-DMF-SO₃H is probably explained in terms of the negligible solubility of the sodium salt and the inertia of the heterogeneous acid catalyst in EtOH (95%). It should be noted that the accumulation of sodium salt and insoluble substances generated in the transformation may suppress the reaction rate. For this reason, a longer time than 6 h is needed to convert the reactants completely at the 7th recycle.

Conclusions

HCP-based polar materials, HCP-DMF and Two HCP-DMF-SO₃H, were prepared by hypercrosslinking of DMFcontaining monomers. The creation of a DMF-like microenvironment and the enhanced polarity of HCP-DMF was disclosed by FT-IR and fluorescence spectra. These two HCP-based materials exhibited quite a good performance in assisting the conversion of NaN3 to benzylic azides and the synthesis of 1,2,3-triazoles. In all the reactions, ethanol was used as the solvent, avoiding the utilization of hazardous DMF solvent. The polar HCP-based materials can be easily recycled as well. The DMF moieties in these two materials played a crucial role in ensuring a good performance in the model reaction. On the basis of this work, it is conceivable that the task-specific decoration of heterogenous catalysts with accessible solvation microenvironments and high surface areas may be a new facet of green catalysis and synthesis. This type of topic for material design can contribute not only to eliminating the use of hazardous solvents but also to enhancing catalytic performance through synergistic catalytic effect.

Conflicts of interest

There are no conflicts to declare.

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