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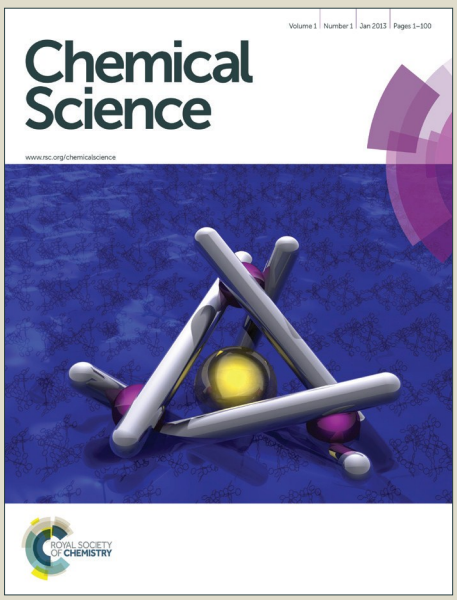

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EDGE ARTICLE

Photochromic Metal-Organic Frameworks for Inkless and Erasable Printing

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Inkless and erasable printing is the key answer towards a sustainable paper industry. It's the solution for reducing paper wastages and the associated environmental hazards from the waste paper processing. However, only a few cases have been reported in the literature where inkless printing has been tested with some systems. In an attempt to address this solution, we have used photochromic metal organic framework (MOF) and tested the capability as inkless and erasable printing media. The printing has been performed by using sunlight as the light source on MOF coated papers. The resultant printing has a good resolution, stability, capable of being read both by human eyes and smart electronic devices and the paper can be reused for several cycles without any significant loss in intensity. Interestingly, different coloured printing with similar efficiency was achieved by varying the structure of the MOF.

Introduction

Photochromic materials are capable of changing their colour when exposed to light. Such photochromic materials contain spiropyran, diarylethene, azobenzene or redox active cores in their structures[1] which are responsible for the colour change. These materials have been extensively used for making photochromic glasses, lenses, and filters because of their interesting reversible colour change property.[2] Moreover, these materials have also been proposed for applications like erasable and inkless printing, 3D data storage, etc.[2] Inkless and erasable printing is one of the key solution to the environmental problems arising because of the ever increasing usage of printed contents. Inkless property is necessary to reduce the cost and environment hazards arising from the usage of inks. Reusability of the printing media is another solution for reducing the paper wastes arises out of printing for temporary purpose. In combination, potential solution towards sustainability is the use of a media which wouldn't require any ink for printing and could be used over cycles. Although thermal printing is a traditional method for inkless and erasable printing, because of high energy consumption and sensitivity towards minute heat generation, there is a search for other techniques. Use of photochromic media for addressing media can be of potential interest for this problem, however, conventional photochromic materials have short lifetime and return to the initial colour within a few minutes of excitation. This fast reversibility of these photochromic materials limit them to be used as media for inkless and erasable printing where the printed content would be vanished in the background. Thus, it is impractical to use those materials as a media for inkless and erasable printing. To avoid such circumstances, the necessary conditions to design a practical erasable printing media are: (i) their ability to retain the photogenerated colour for a prolonged period of time so that the content remains legible/readable; (ii) the reversibility of this colour change so that the same paper can be used for multiple cycles, and (iii) the intactness of the colour in presence of paper contents. Thus, there is a constant search for a suitable photochromic material which can fulfil all the above mentioned requirements and can be used for practical applications in inkless and erasable printing media.[3]

Herein, we report three different metal organic frameworks (MOFs)[4] constructed from co-ordination between alkaline earth metal ions and ligands containing photochromic 1,4,5,8-naphthalenediimide (NDI) core[5] and their application for inkless and erasable printing. NDI has a redox active core and can exhibit reversible photochromism when suitable substituents are attached. In order to avoid the fast decolouration of NDI containing chromophores, we have incorporated this NDI core inside the extended structure of MOFs.[6] We believe that because of the formation of this extended structures and the additional interactions, photochromic behaviour of the NDI core changes abruptly as compared to the discrete NDI units and the system becomes suitable for application as inkless printing media.[3]

Results and Discussions

All the MOFs reported in this paper have been synthesized by the solvothermal reactions between the organic BINDI linker (Figure 1a) and the corresponding metal salts. All these

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Electronic Supplementary Information (ESI) available: [Contains Detailed synthetic procedures, PXRD, FT-IR, TGA, crystallographic data (CIF) and other characterization data]. See DOI: 10.1039/x0xx00000x

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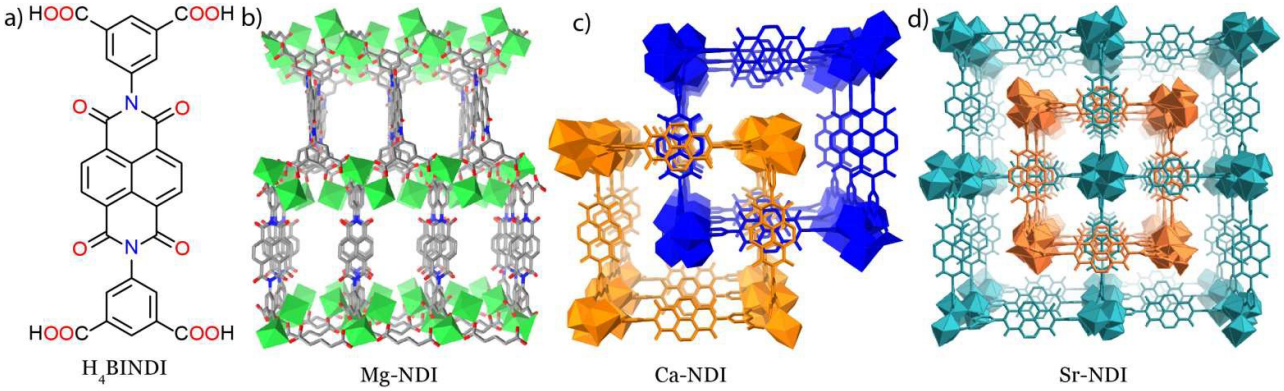

Figure 1. (a) Chemical diagram of H_4BINDI ligand; Crystal structure for (b) Mg-NDI, (c) Ca-NDI and (d) Sr-NDI. Mg-NDI shows 3D structure while for the other cases, two nets interpenetrate forming a two-fold interpenetrated structure.

MOFs have 3D extended structure (Figure 1b, 1c, 1d) where metal ions are co-ordinated to the 4 carboxylate groups of the organic ligand. Mg-NDI, crystallizes in *P*2/*c* space group with two different types of co-ordination environment around the Mg(II) centers. Such co-ordination makes the parallel orientated NDI moieties separated by a distance of 7.1 Å. Rectangular shaped channels [10.9×7.1 $Å^2$] were generated inside the Mg-NDI structure and the wall of these channels were constructed from NDI moieties (Figure S3). Ca-and Sr-NDI crystallize in $I4_1/a$ space group and differ structurally from Mg-NDI. Both Ca- and Sr-NDI are isostructural and in the extended framework, two equivalent nets were interlocked via π-π stacking between adjacent NDI moieties forming a 2-fold interpenetrated structure (Figure 1c, 1d). In this case, the NDI moieties of the 2nd net align in a perpendicular orientation compared to the 1st net, during the interpenetration (Figure S5). PXRD patterns of the as-synthesized MOFs indicates bulk phase purity of the as-synthesized materials (Figure S6 and S7). FT-IR analyses for the MOFs shows that additional peaks appear at 2918 and 2846 cm^{-1} in comparison to free ligand; corresponding to the formation of new M–O bonds (Figure S8). The weakly co-ordinating solvents present in the Mg-NDI framework were released around 150 °C temperature, as evidenced from the TGA plots (resulting in 17% weight loss) of the dried MOF samples and the frameworks eventually decompose at 550 °C (Figure S12).

As-synthesized Mg-NDI is light yellow in colour while the other MOFs are found to be almost colourless. When these dried MOF crystals were exposed to intense sunlight for 60 seconds, a drastic colour change occurred for all the MOFs, revealing their photochromic nature (Figure 2a). The colour of these irradiated materials was found to be dependent on the structure of the MOF. Mg-NDI turned into brownish black colour after the sunlight irradiation, while the isostructural Ca-, and Sr-NDI MOFs turned into green colour after similar treatment. This colour change causes the generation of new additional peaks in the UV-vis spectra [630 and 740 nm centered broad peak for Mg-NDI, Figure 2b; 620 and 605 nm centered peak for Ca- and Sr-NDI, respectively; Figure S13 and S14]. The observed PXRD patterns (Figure S6 and S7) indicate that these MOFs retain their initial structure even after the photochromic transformation and corresponding quenching. FT-IR spectra of all the MOFs were also found to be identical for the cases of non-radiated, radiated and quenched materials, again suggesting the retention of functional groups and the bonding during this photochromic changes (Figure 2c). Apart from the internal structure, the external morphology of Mg-NDI was also retained after sunlight irradiation, as evidenced from the SEM images (Figure 2e and 2f).

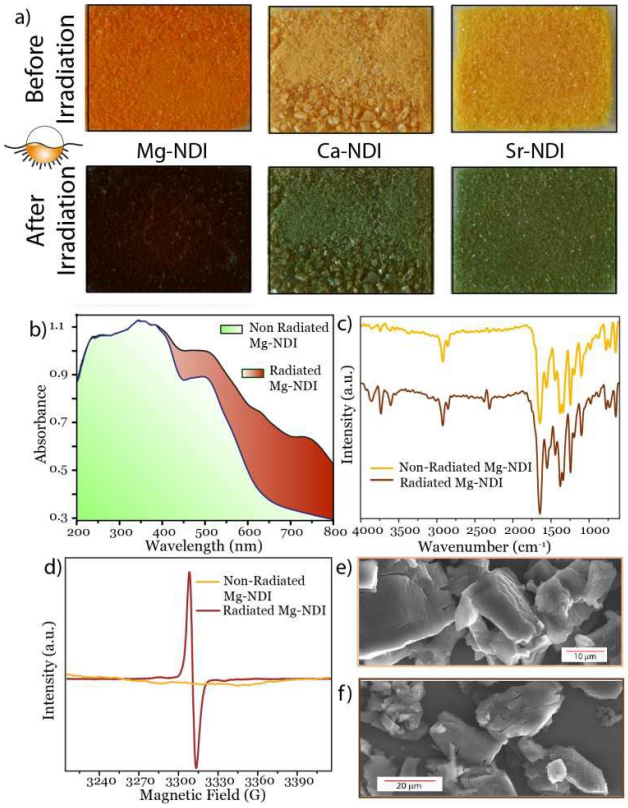

Figure 2. (a) Colour changes of pristine MOF materials under sunlight irradiation showing photochromic property; change in (b) UV-vis spectra, (c) IR spectra (d) EPR spectrum, and SEM image (e) before and (f) after sunlight irradiation on Mg-NDI.

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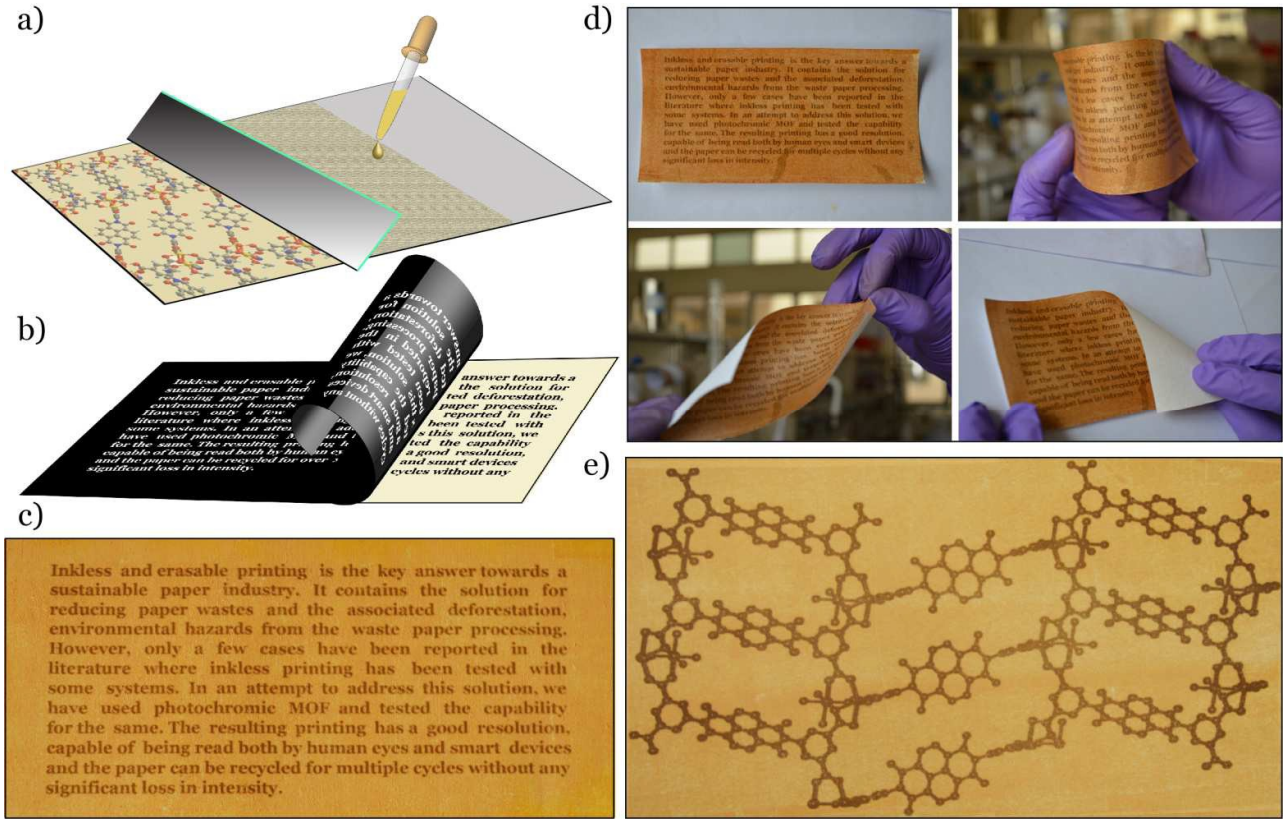

Figure 3. (a) Schematic representation for preparation of Mg-NDI coated paper; (b) scheme for printing on the coated paper with stencil and sunlight; (c) test for resolution of the printed content by printing of letters on a 11.5x5.4 cm^2 paper; (d) test for mechanical deformation with Mg-NDI coated paper and (e) image showing ball and stick model of Mg-NDI structure on the Mg-NDI coated paper having dimension of 14.9x8.1 cm^2.

It is well documented in the literature that because of the *n*-type character, under suitable conditions NDI moiety undergoes one electron transfer and get converted into a NDI radical species (NDI•).[7] This NDI• can be generated from neutral NDI via various methods like chemical, photochemical and electrochemical treatment.[8] NDI• bears a characteristic EPR signal at g = 2.002–2.004 region, originating from the unpaired electron.[9] This unpaired electron from NDI• gets quenched readily when comes in contact with paramagnetic species like like oxygen gas.[7] Use of alkaline earth metal ions as nodes for construction of Mg-, Ca- and Sr-NDI keep the unpaired electron of the radical species unaffected due to the absence of partially filled d-orbital. EPR studies revealed that as- synthesized MOFs are silent to the applied magnetic field while a sharp singlet peak appeared for the case of sunlight radiated MOFs with g= 2.003 (Figure 2d, S16 and S17). This signal accounts for the formation of NDI• radical species upon sunlight radiation which vanishes when the materials are quenched and returned to their original colour. It is noteworthy that after sunlight irradiation BINDI ligand also shows similar signal [g= 2.004, Figure S18] in the EPR spectrum; indicating the generation of NDI• species in its structural backbone. However, this radical generation requires a prolonged irradiation time [10 min] followed by quick loss of photogenerated colour [reverts to original colour in <2h, Figure S20], indicating a shorter lifetime [compared to 12h for Mg-NDI] for the generated radical species. It was found that the colour of the radiated material has a poor contrast compared to the non-radiated one, thus making BINDI non-suitable for inkless and erasable printing applications. This short lifetime of the BINDI radical species is a result of short π-π stacked NDI cores, which are located at a separating distance of 2.6 Å, as evidenced from its crystal structure (Figure S4). Stacking between the adjacent NDI cores facilitates the quenching of NDI• through the transfer of electrons to the neighbouring moieties. As a result, the photogenerated colour becomes transient and quickly reverts to its initial colour. Interestingly, these NDI cores are separated by a distance of ~ 7.1 Å for Mg-NDI, which eliminates the chance of π-π stacking among those moieties and brings stability to the NDI• radical species (Figure S3). It has been evidenced in literature that the mobility of the radical electron from the NDI core enhances in the solid statewhen they are perfectly stacked over each other. But, when the stack is removed by solubilising in proper solvent, the transport of the electron is hampered. Thus, the localization of the radical has been achieved by separating the NDI cores in solution.[8a, 10] In case of isostructural Ca- and Sr-NDI MOFs, the π-π stacking distance between the adjacent NDI moieties is 2.4 Å. However their orientation is orthogonal to each other (Figure S5). And because of this orthogonal

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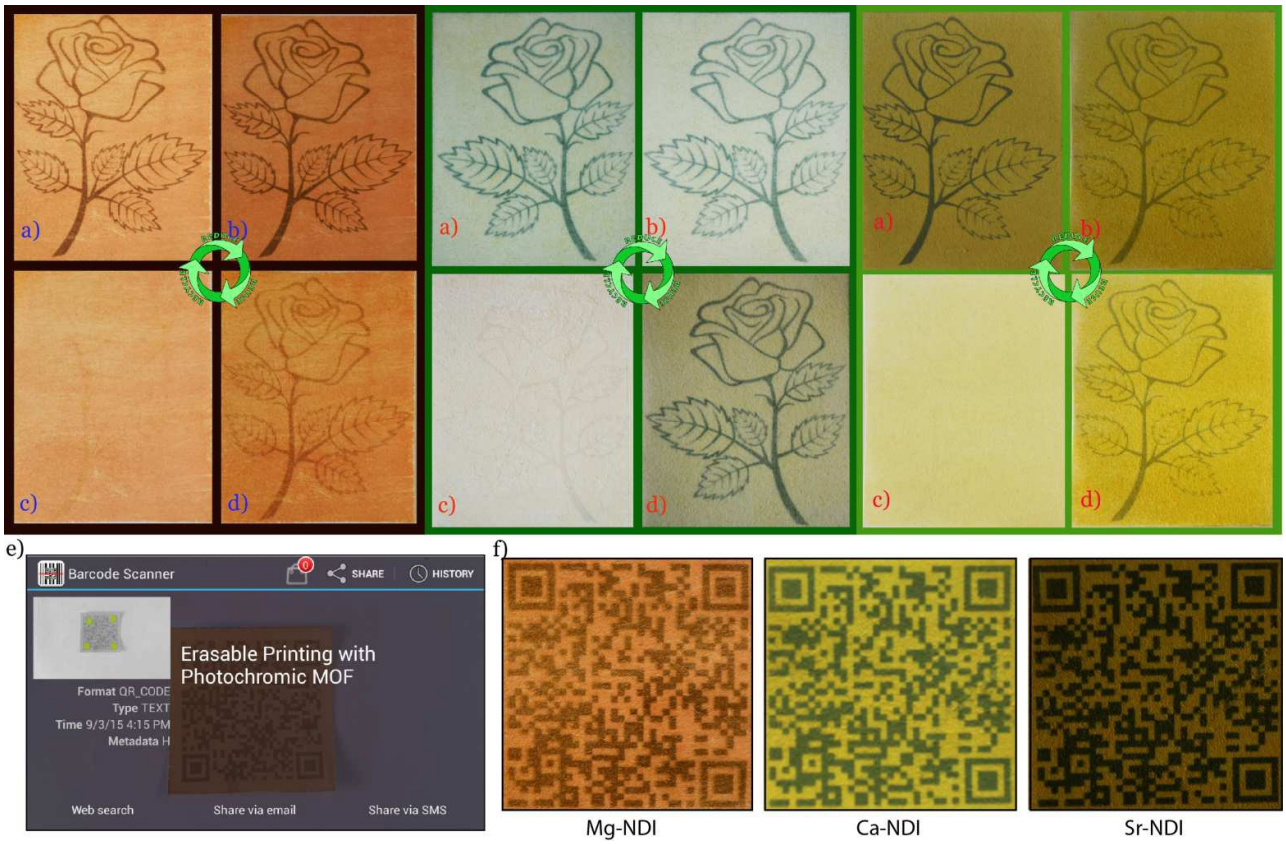

Figure 4. (a) Photograph of a content printed on Mg-NDI coated paper; (b) content after 12 h of printing; (c) self erased paper after keeping in the dark for 12 h; (d) photograph of the paper after printing for 4th round; (e) Detection of a QR code printed on the Mg-NDI coated paper with a smartphone; (f) QR code printed on Mg-NDI, Ca-NDI and Sr-NDI coated paper showing different coloured printing.

orientation, radicals cannot be quenched via transport mechanism as it happens in the bare BINDI ligand. Thus the photogenerated NDI• within the MOF backbone attains stability. The nature of the photogenerated radical [singlet peaks centred at g= 2.003] was found to be same for all the MOFs (Figure S19) and bare BINDI ligand.

Noting this interesting photochromic property of these NDI based MOFs, we planned to use them as inkless and erasable printing media. The MOF coated paper was prepared by drop casting an ethanol suspension of finely powdered Mg-NDI on a cellulose filter paper followed by surface smoothening with a glass slide (Figure 3a). The paper was then dried under vacuum where the coating was adhered to the paper, without losing the flexible nature of the resulting coated paper (Figure 3d). The printing of the contents on this coated paper was performed by controlling the incidence of sunlight through a stencil. The stencil was prepared by printing an inverted object of the desired content on a transparent polyurethane sheet (Section S14 in ESI). The printing surface of the coated paper was then covered with the stencil and the assembly was kept in the intense sunlight (having flux 100 mW/cm^2) for less than 60 seconds. After this exposure, the stencil was removed from the top of the coated paper to obtain the content printed in brownish black colour on pale yellow background of Mg-NDI (Figure 3b). Large scale text printing was tested with a stencil of 11.9 x 5.4 cm^2 sized print obtained with a similarly designed stencil. No overlap among the 610 characters occupied in 10 lines was observed and each of the characters was clearly distinguishable from its next neighbour (Figure 3c). The colour contrast between the foreground and background was found be well enough for visual reading of the content. This visual legibility was again confirmed from an outline sketch having dimension of 14.9 x 8.1 cm^2. The objects present in the drawing are well-defined in respect to their constituent lines and the printed content can be easily visualized (Figure 3e). Similar printing with Ca- and Sr-NDI coated paper gives excellent legibility where the resulting content was printed in dark green colour.

The printed content was found to disappear into the background after 24h for the cases of Mg-, Ca-, and Sr-NDI coated papers, converting them into a blank paper which can be used for next round of printing and as shown in figure 4d, the intensity of the 4th round printed content remain comparable as the 1st round, though some loss in contrast with background is observed because of repeated cycles. As the printed content is kept in ambient atmosphere, aerial oxygen diffuses through the excited material converting it back to the initial state. Time required for complete quenching of the excited material along with complete reversal to the initial colour was found to be 24h. Thus the printed content

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remained legible for long period of time (Figure 4c), enough for temporary uses. It is noteworthy that, erasing of this printed paper can be accelerated for re-use during this 24h period by flushing oxygen gas on the printed paper. Thus, reversibility and recyclability of the printing media has been successfully established.

Apart from the naked eye legibility of the printed content, the resulting printing was found to have enough resolution to be recognized by smart devices. 1D and 2D barcodes were printed on the Mg-, Ca- and Sr-NDI coated papers using an identical stencil, to confirm the ability to be decoded by smart devices. A version-5 QR code (containing 37 rows and 37 columns) with a dimension of 4.7 x 4.7 cm^2 was prepared which contained 39 characters (Figure 4f). The embedded code 'Erasable Printing with Photochromic MOF' was readily decoded with any reader software installed on smart electronic devices, as shown in figure 4e. Similar quick response was also found for the case of 1D barcodes (Figure S23), proving the excellent machine legible nature of the printed content on the Mg-NDI coated paper. UV-vis study of the printed and erased papers over multiple cycles (Figure S15) showed that the colour intensity of Mg-NDI in both coloured and colourless form hold steady for 04 cycles.

Conclusions

In conclusion, we have demonstrated a novel approach to develop an inkless and erasable printing media using photochromic MOFs. Precise impression of the desired content on the printing media has been achieved by controlling the incidence of sunlight on the media with a stencil and without use of any ink. Further, the resulting print is well-recognized by smart electronic devices as well. The printed content was self-erased after 24h, without using any other external stimuli like heat, or UV light. The self-erasing nature makes the system suitable for performing several printing-erasing cycles with the same paper, making the printing process cost-effective and environmental friendly. Additionally, we can tune the colour of printing by selection of different MOFs, having different structures. Development of new material capable of showing multicolour-photochromic behaviour for application in colour printing is underway in our laboratory.

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The synthesis and photochromic property of Mg-NDI and Ca-NDI was previously reported by us[11] and by Han *et al*[12], respectively.

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