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Photodimerization induced Photomechanical behaviour in Alkyldiammonium Salts of *trans*-Dichlorocinnamates: Exploration of [2+2] Reactions in as Synthesized Salts, Single Crystals and Organogels

Shaheen Sultana, Debasis Pal, Kumar Biradha*

The development of light-responsive molecular crystals that convert light into mechanical energy is a burgeoning field with applications ranging from remote actuation to flexible electronics. This study explores the [2+2] photodimerization and subsequent photomechanical behaviour of a series of organic salts synthesized from alkyldiamines ($H_2N\text{-}(CH_2)_n\text{-}NH_2$, n= 2-4) B_n and *trans*-2,4/3,4-dichlorocinnamic acid (A_{m4}, m =2-3). By employing chloro-substitution to direct crystal packing into photoreactive β-type structures, we investigated these reactions across three distinct states: as-synthesized salts, single crystals, and supramolecular organogels. Experimental results demonstrate that salts containing ethylenediamine ($B_2(A_{24})_2$) and propylenediamine ($B_3(A_{24})_2$) are photoactive across all states, while butylenediamine ($B_4(A_{24})_2$ & $B_3(A_{24})_2$) derivatives remain photoinactive. Notably, the [2+2] reaction in single crystals of $B_2(A_{24})_2$ and $B_3(A_{24})_2$ induced dramatic photomechanical effects, including macroscopic bending, surface peel, and the formation of surface cracks. The successful formation of cyclobutane dimers was confirmed *via* ^{1}H-NMR, MALDI-ToF mass spectra, and single-crystal X-ray diffraction. Furthermore, we report a rare instance of organogels derived from these simple organic salts undergoing [2+2] photodimerization while exhibiting significant electrical conductivity ((5.2×10^{-3} S cm^{-1}). Additionally, certain salt compositions demonstrated high efficiency for iodine absorption. This work highlights the versatility of organic diammonium salts as multifunctional materials for optomechanics, sensing, and conducting soft materials.

Introduction

The transformation of light energy into mechanical energy in molecular crystals is a rapidly advancing research area, harnessing solid-state reactivity to produce rapid, efficient movements in remote actuation, artificial muscles, microdevices, and flexible electronics.[1-5] Light-responsive crystalline materials exhibit dynamic mechanical responses such as fracturing,[6] twisting,[7] jumping,[8,9] or bending,[10,11] often arise from rapid structural changes and internal strain accumulation within the crystal lattice. Photomechanical deformations are primarily attributed to photochemical reactions or photoisomerization occurring within crystals. Classic examples include [2+2] photodimerization[12] of olefins and [4+4] photodimerization of anthracenes.[13-15] Some organic solids, metal complexes and coordination polymers exhibit photomechanical motions so intense they lead to explosions or shattering, akin to popcorn popping on a hot plate.[16-20] Vittal and co-workers have extensively studied the photomechanical effect associated with [2+2] photodimerization of 4-styrylpyridine[21,22] and 1,2-di(4-pyridyl)ethylene.[23] Bardeen *et al.* demonstrated photomechanical deformation in crystalline materials *via* the [4+4] photodimerization of 9-tert-butylanthroate (9-TBAE) nanorods.[24] More recently, Biradha and co-workers reported [2+2] photopolymerization in single crystals of flexible dienes, which induced significant bending of the crystals.[25] In addition to crystalline solids, soft materials such as polymers,[26] hydrogels,[27] and liquid crystals also exhibit photomechanical properties.[28] Despite the remaining fundamental and practical hurdles, emerging uses of soft robotics, optoelectronic materials, and optical switches demonstrate the significant potential for photomechanical crystals in upcoming technologies. However, studies of photomechanical properties in crystals offer valuable insights into their internal response mechanisms given the availability of their precise structural information.

Several crystalline organic solids are being deliberately designed to achieve topochemical [2+2] cycloaddition reactions by precisely controlling intermolecular forces and molecular packing arrangements.[29] Carboxylate salts of organic amines are extensively employed for screening functional organic crystalline materials, including host-guest crystals,[30] crystalline-state photoreactions,[31,32] topochemical polymerizations,[33] and organogelators.[34] Organic salts offer key advantages given their simple preparation and the creation of the materials containing strong charge assisted hydrogen bonds. A notable example of carboxylate salt of amine was reported by Ramamurthy and coworkers where light triggers large molecular

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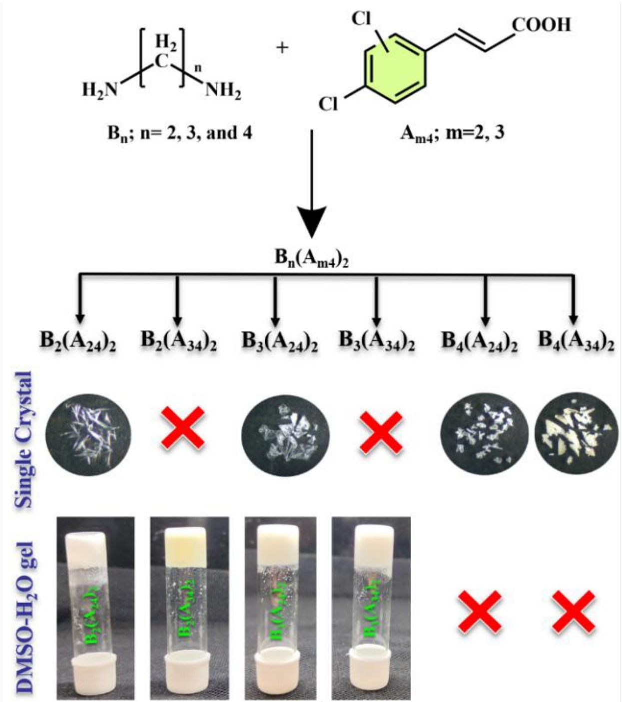
motions in the crystals. In this example, irradiation of a double salt formed between 1,2-*trans*-diaminocyclohexane and *trans*-2,4-dichlorocinnamic acid results in mirror symmetric β-truxinic acid *via* pedal motion of the olefins in the solids.[35] Further, salts of cinnamic acid with series of alkyl diamines (H_2N-$(CH_2)_n$-NH_2, n= 2-6) were also shown to undergo [2+2] reaction upon irradiation.[36,37] Furthermore, crystalline organic salts have gained interest for applications in gas capture,[38] catalysis,[39] conductivity[40] and molecular separations.[41] Recently, Cooper *et al*. reported isoreticular ammonium halide salts as potential alternatives to porous metal-organic frameworks (MOFs), showing promising high level iodine capture efficiency at 70 °C.[42] On the other hand, primary ammonium monocarboxylates were shown as low-molecular-weight gelators (LMWGs) *via* the formation of one-/two-dimensional hydrogen-bond networks.[43] In these soft materials, one-dimensional anisotropic interactions restrict lateral fiber growth, producing highly branched one-dimensional fibers that entangle to form a three-dimensional network, thereby immobilizing the solvent.[44] In addition, gels provide versatile platform for the promotion of many organic reactions involving covalent bond formations.[45] We have shown earlier that [2+2] dimerization and polymerization reactions progress smoothly both in organogels (OGs) and metal-organic gels (MOGs).[46-49] However, a supramolecular organogel derived from simple organic salts capable of [2+2] photodimerization isn't reported till date.

Herein, we have exploited the strategy of salt formation between alkyl diamines (H_2N-$(CH_2)_n$-NH_2, n= 2-4) B_n and two monocarboxylic acids namely *trans*-2,4/3,4-dichlorocinnamic acid (A_{m4}, m =2-3) to study the photodimerization reactions in the as synthesized salts, single crystals as well as organogels (Scheme 1). The chloro-substitution on the aromatic ring of cinnamic acids is anticipated to direct the packing to β-type structures which promotes [2+2] reactions (Scheme S1).[50-52] Among the six possible combinations, the crystals suitable for single crystal diffraction analysis were obtained for $B_2(A_{24})_2$, $B_3(A_{24})_2$, $B_4(A_{24})_2$ and $B_4(A_{34})_2$. All the as synthesized salts of B_2 and B_3 found to exhibit [2+2] reaction upon irradiation whereas B4 salts are photoinactive. The similar reactivity is also observed in their respective single crystals. Interestingly, the [2+2] reaction in the crystals of $B_2(A_{24})_2$ and $B_3(A_{24})_2$ accompanied bending, fragmentation and development of cracks on crystal surface. ^{1}H-NMR, Matrix-Assisted Laser Desorption Ionization analysis (MALDI-ToF) and single crystal structures confirmed formation of photo-dimers. Among the six possible combinations, four combinations, namely B_2A_{24}, B_2A_{34}, B_3A_{24} and B_2A_{34}, able to form organogels both in protic and aprotic solvents, owing to their extensive hydrogen-bonded network and good solubility. Organogels also found to undergo [2+2] photodimerization upon irradiation. Further, the gels found to show significant electrical conductivity (5.2×10^{-3} S cm^{-1}) as well. The as-synthesised B_3 and B_4 salts of A_{m4} exhibited excellent ability for iodine absorption.

Results and Discussion

The *trans*-2,4/3,4-dichlorocinnamic acids (A_{24}/A_{34}) were synthesised using Knoevenagel condensation reaction between 2,4/3,4-dichloro benzaldehyde and malonic acid.[35] The ammonium salts were synthesized by reacting two equivalents of alkyl diamine ($B_{2\text{-}4}$) with one equivalent of cinnamic acid (A_{24} or A_{34}) in methanol at ambient temperature, yielding the salts in nearly quantitative amounts (Figure S1; ESI). Crystals suitable for single-crystal X-ray diffraction (SCXRD) analysis were obtained *via* slow evaporation from suitable solvents (Scheme 1 & Table S1; ESI) in 3-4 days. Despite of our best efforts, diffraction-quality single crystals of $B_3(A_{34})_2$ and $B_3(A_{34})_2$ could not be obtained. The single crystals of $B_2(A_{24})_2$ & $B_2(A_{34})_2$ are found to be photoreactive upon exposure to 365 nm UV light. Notably, after few hours of irradiation $B_2(A_{24})_2$ crystals exhibited visible bending, while $B_3(A_{24})_2$ crystals displayed visible cracks and surface peeling, known as photomechanical behaviour.

SCXRD analysis revealed that $B_2(A_{24})_2$ crystallise in monoclinic *P*2$_1$/*c* space group, whereas $B_3(A_{24})_2$ crystallise in orthorhombic *Pbca* space group. The asymmetric units of both the salts contain two units of 2,4-dichlorocinnamate anions and one unit of corresponding diammonium cation (disordered site occupancy in case of propane diamine). $B_2(A_{24})_2$ contains two additional water molecules in its asymmetric unit as well. Carboxylate anions involved in charge-assisted N-H···O hydrogen bonding with alkyl diammonium cations (Figure 1a, c). Two carboxylates of $B_2(A_{24})_2$ form four N-H···O hydrogen bonds with ethylenediammonium cation (N···O: 2.765(6) Å-3.203(7) Å; <N-H···O: 128°-172°). In contrast, in $B_3(A_{24})_2$, the carboxylates form total seven N-H···O hydrogen bonds with the propanediammonium cation (N···O: 2.711(7) Å-3.121(7) Å; <N-H···O: 102°-166°, Table S2; ESI). Such type of hydrogen-bonding generates two-dimensional layer with dangling dichloro-aromatic groups on one side of the layer.



Scheme 1. Representation of molecular structures and corresponding alkyldiammonium salts studied herein, along with photographs of their single crystals and organogels. The materials failed to produce good quality single crystals or gels are represented with a cross.

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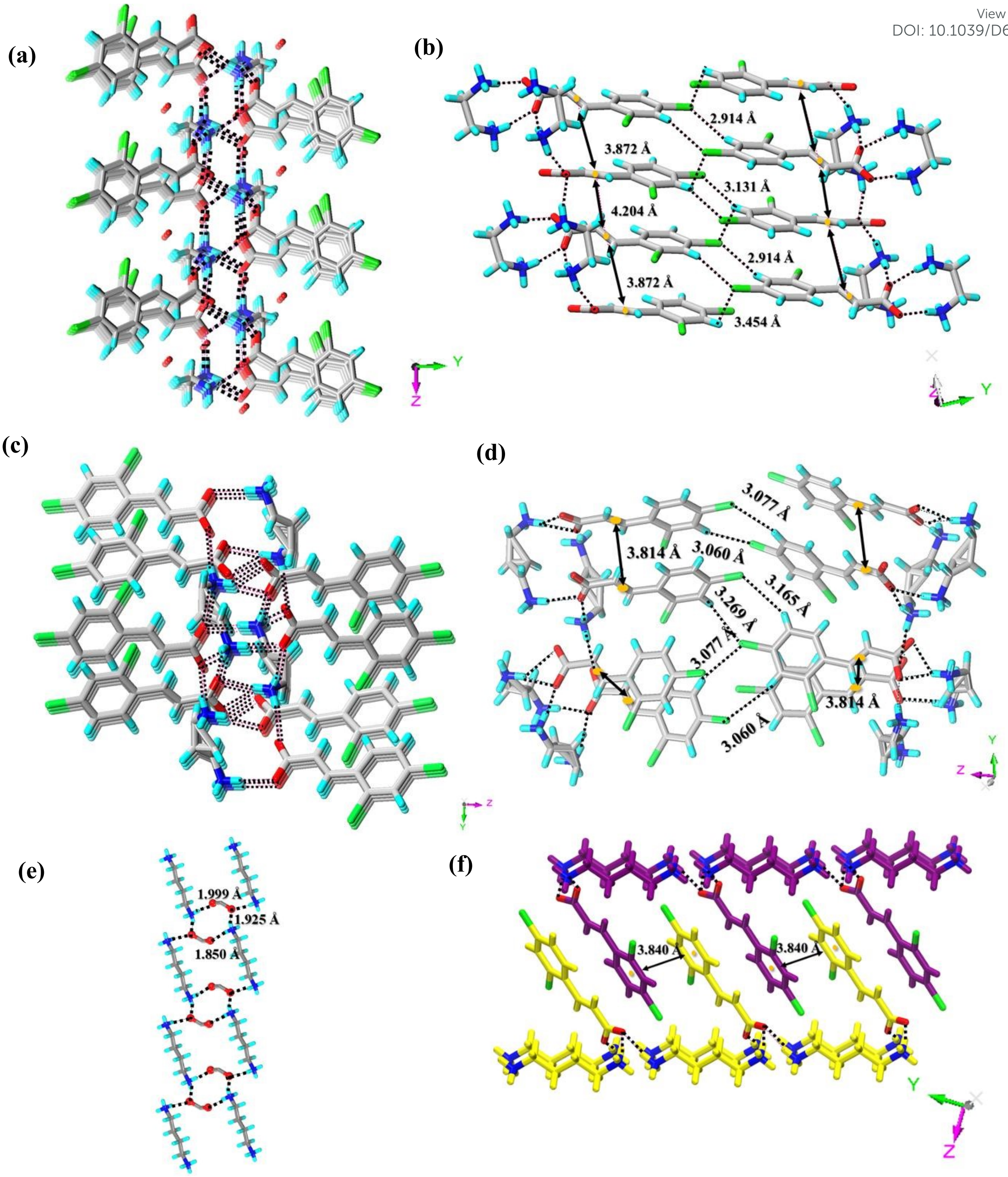

Figure 1. Illustrations for the crystal structures of $B_2(A_{24})_2$, $B_3(A_{24})_2$ and $B_4(A_{24})_2$: bilayer type of hydrogen bonding in (a) $B_2(A_{24})_2$ and (c) $B_3(A_{24})_2$; alignment of double bonds and Cl…Cl interactions in (b) $B_2(A_{24})_2$ and d) $B_3(A_{24})_2$; (e) hydrogen-bonded layer and (f) interdigitation of cinnamate anions in the packing of the layers in $B_4(A_{24})_2$.

The layers pack to form a bilayer structure of alternating hydrophilic and hydrophobic layers (Figure S3). The hydrophobic layers interact with each other by abundant C-H···Cl (Table S2; ESI) and type II Cl···Cl (Table S3; ESI) interactions.[53] The water molecules in $B_2(A_{24})_2$ form two O-H···O hydrogen bonds with carboxylate anion and one O-H···O hydrogen bond among themselves (Table S2; ESI). In both the structures, the olefinic double bonds are found to have reactive alignment with distances of 3.872 Å and 4.204 Å in $B_2(A_{24})_2$ and 3.814 Å in $B_3(A_{24})_2$ (Figure 1b, d). The powder X-ray diffraction pattern (PXRD) of the as-synthesised $B_2(A_{24})_2$ and $B_3(A_{24})_2$ salts agree well with the simulated pattern of their single crystals (Figure S2; ESI).

The crystal structure analyses of $B_4(A_{24})_2$ and $B_4(A_{34})_2$ revealed that both are isostructural and crystallise in *P*-1 space group. The asymmetric units contain one unit of corresponding

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dicholocinnamate and half unit of 1,4-diammonium butane which displays all-anti conformation in both cases with dihedral angles of 178°-178.9°. The hydrogen bonding between carboxylates and alkyl diammonium cations (N···O: 2.770(3) Å-3.405(3) Å; <N-H···O: 155°-174° for $B_4(A_{24})_2$ and N···O: 2.752(4) Å- 3.285(5) Å; <N-H···O: 136°-168° for $B_4(A_{34})_2$) leads to the formation of hydrogen bonded layer (Figure 1e) with dichlorocinnamate groups projecting from both sides of the layers. The layers pack such that there is interdigitation of cinnamate groups which supported by $\pi\cdots\pi$ interactions between the cinnamates with head-to-tail stacks and C-H···Cl and Cl···Cl interactions (Figure 1f). The head-to-tail stacking of the cinnamates places the C=C bonds beyond the [2+2] reactive distance.

The gelation experiments were conducted with all six as-synthesized materials in three different solvent systems. Four of the six materials were found to form gels, while $B_4(A_{24})_2$ and $B_4(A_{34})_2$ (Table S4; ESI) did not. The three successful solvent systems for gelation are found to be DMSO, DMSO/water and nitrobenzene. While $B_2(A_{24})_2$ demonstrated robust gelation across all three solvent systems, $B_2(A_{34})_2$ formed stable gels only in DMSO and DMSO/water. Furthermore, its nitrobenzene gel was significantly weaker, failing to maintain its own weight after few minutes. $B_3(A_{24})_2$ and $B_3(A_{34})_2$ only form stable gels in DMSO/water. The gelation process was confirmed from inverted vial test and they exhibit critical gelation concentration (CGC) of 10-20 mg ml^{-1}. The organogels display thermo-reversible nature. The oscillatory shear experiments, including amplitude and frequency sweeps, were conducted at room temperature to investigate the viscoelastic properties of these gels.

First, seven organogel samples were sheared in strain sweep experiments with a constant frequency of 10 rad s^{-1} (amplitude sweep experiment) to determine the linear viscoelastic range or limiting strain (σ_y) for performing the frequency sweep experiments (Figure 2a,c & S4; ESI). Frequency sweep experiments were carried out under 0.1 % strain, as suggested by amplitude sweep experiments. In all cases, the values of the storage or elastic modulus (G') were larger than that of the loss or viscous modulus (G'') and they were frequency invariant over the entire range of angular frequency, ω (Figure 2b,d & S4; ESI); this revealed typical viscoelastic behaviour. The aqueous-DMSO gel of $B_2(A_{24})_2$ was found to be the strongest (G'-G''≈750 kPa) of all the gels studied herein (Table 1). The high-resolution transmission electron microscopic (HRTEM) images of the aqueous-DMSO gel mostly showed a popsicle stick like morphology for $B_2(A_{24})_2$, $B_2(A_{34})_2$ and $B_3(A_{24})_2$ whereas both FESEM and HRTEM images displayed a plate kind of morphology for $B_3(A_{34})_2$ gel (Figure 2e-h & S5; ESI). The PXRD patterns of aqueous-DMSO xerogels were compared with the single crystals and as-synthesised gelator salts. As shown in Figure S6, diffraction peak matches well in all cases except for $B_2(A_{34})_2$, indicating that the xerogel typically possesses the same phase with as-synthesized material.

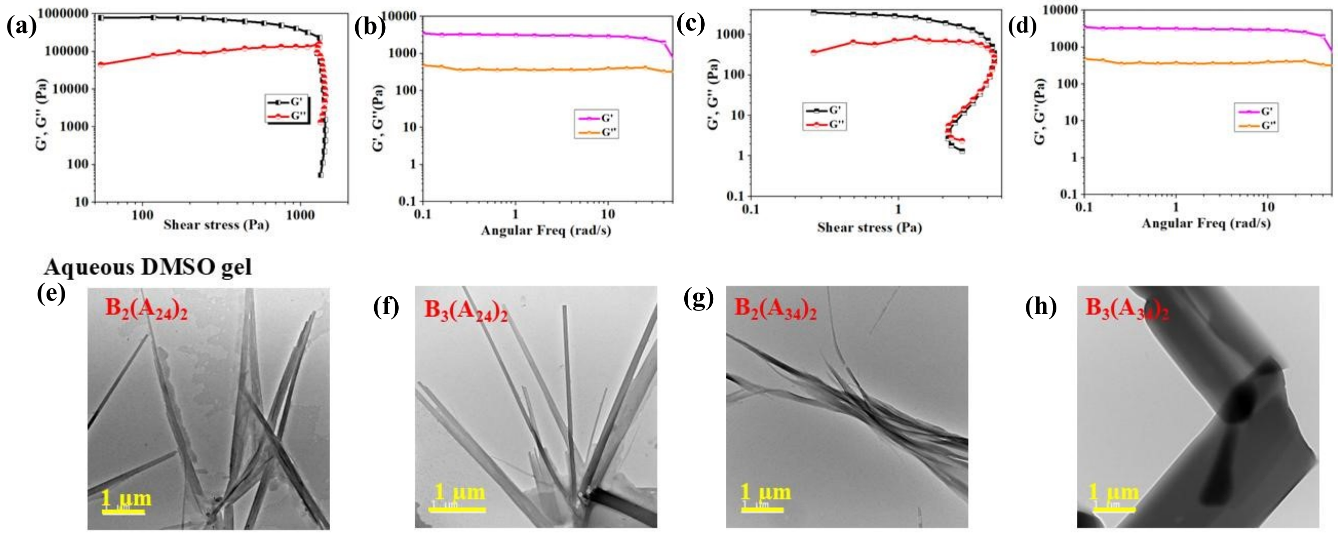

Figure 2. Illustrations for the rheological measurements of aqueous-DMSO gels of $B_2(A_{24})_2$ (strongest) and $B_3(A_{34})_2$ (weakest): (a, c) amplitude sweep, (b, d) frequency sweep; (e-h) HRTEM images displaying different morphologies.

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Table 1 Yield stress (σ_y), rigidity (G'-G'') and morphology of various organogels.

Gel	Yield stress (σ_y Pa)	G'-G'' (Pa)	Morphology
$B_2(A_{24})_2$ (aqueous-DMSO)	1300	754,280	Popsicle stick
$B_2(A_{24})_2$ (DMSO)	160	53,710	Popsicle stick
$B_2(A_{24})_2$ (Ph-NO_2)	217	69,186	Oval plate shape
$B_2(A_{34})_2$ (aqueous-DMSO)	47	22,877	Popsicle stick
$B_2(A_{34})_2$ (DMSO)	46	6,910	Scattered Popsicle stick
$B_3(A_{24})_2$ (aqueous-DMSO)	61	21,606	Popsicle stick
$B_3(A_{34})_2$ (aqueous-DMSO)	5	2952	Rectangular plate shaped

The photochemical reactions were carried out on all crystals, as-synthesized materials, and freshly prepared aqueous-DMSO gels by irradiation at 365 nm in a UV chamber. As suggested by the crystal structures, two of the samples underwent near-quantitative photochemical [2+2] dimerization within different time frames, as confirmed by ^{1}H NMR and MALDI-ToF analyses. The ^{1}H NMR spectra show the emergence of head-to-head (HH) cyclobutane peaks at δ value 4.58 and 3.91 ppm for $B_2(A_{24})_2$ and $B_3(A_{24})_2$ (Figure S7 & S10; ESI), indicating the formation of HH-*rctt*-2,4cpcb dimer (cpcb = dichlorophenyl cyclobutane).[32,47] % yield of the photodimerization after 24 of UV irradiation is given in Table 2. Moreover, when as-synthesised material of $B_2(A_{34})_2$ and $B_3(A_{34})_2$ salts were irradiated, they also exhibit cyclobutane peaks at δ value 4.10 and 3.59 ppm corresponding to HH-*rctt*-3,4cpcb (Figure S9 & S11; ESI), indicating successful [2+2] photodimerization. ^{1}H NMR spectra of the irradiated gels suggest all B_2 and B_3 salts underwent [2+2] photodimerization in ~ 28-72% yields within 24 hrs (Figure S7-S11, ESI). Appearance of doublet of doublets at nearly the same chemical shift as crystals confirm head-to-head dimer formation. However, the reactions in the gel state proceeded more slowly compared to the as-synthesized and single crystals. Contrary to few instances where gel-to-gel or gel-to-sol transformation[46-49] leads to quantitative photocycloaddition, the organogels in this study cannot withstand the structural changes during photoreaction due to their weak mechanical rigidity. This result in a loss of 'topochemical control' leading to poorer yields (~20% conversion) compared to the crystalline salts. The formation of the dimer was further confirmed by *m/z* peak at 431.92 in MALDI-ToF analysis (Figure S14; ESI).

Table 2 Photodimerization yields (%) after 24 hours of in crystals, as-synthesised materials and organogels of all the salts

	% Yield		
Salts	As-synthesised	Crystals	Gels
$B_2(A_{24})_2$	~90	~90	~29
$B_2(A_{34})_2$	~85	--	~72
$B_3(A_{2,4})_2$	100	100	~58
$B_3(A_{34})_2$	~85	--	~40

Interestingly, the crystals of $B_2(A_{24})_2$ and $B_3(A_{24})_2$ not only underwent [2+2] dimerization, but also displayed photomechanical behaviour. The needle-shaped crystals of $B_2(A_{24})_2$ (ranges from 0.40 mm x 0.05 mm x 0.02 mm to 1.10 mm x 0.05 mm x 0.02 mm) released the accumulated strain generated during the photoreaction by bending after 15 min of UV irradiation (Figure 3a(i–vi)),[21] a phenomenon typically observed in very fine or thin crystals. However, single crystals of $B_3(A_{24})_2$, (0.80 mm x 0.75 mm x 0.10 mm) develop significant cracks on the surface (few µm wide) (Figure 3b(i-vi)) and experience surface peeling effect (Figure S15(i-iv); ESI) after prolong UV exposure. The bending and morphological changes of the crystals of $B_2(A_{24})_2$ and $B_3(A_{24})_2$ upon irradiation are well supported from field emission scanning electron microscopy images (FESEM, Figure S16; ESI) and atomic force microscopy (AFM) images (Figure 3e,f, S17; ESI). AFM height profile exhibits much increased average roughness (*Ra*) [13.8 nm for $B_2(A_{24})_2$ and 46.8 nm for $B_3(A_{24})_2$] parameter for dimer crystals.

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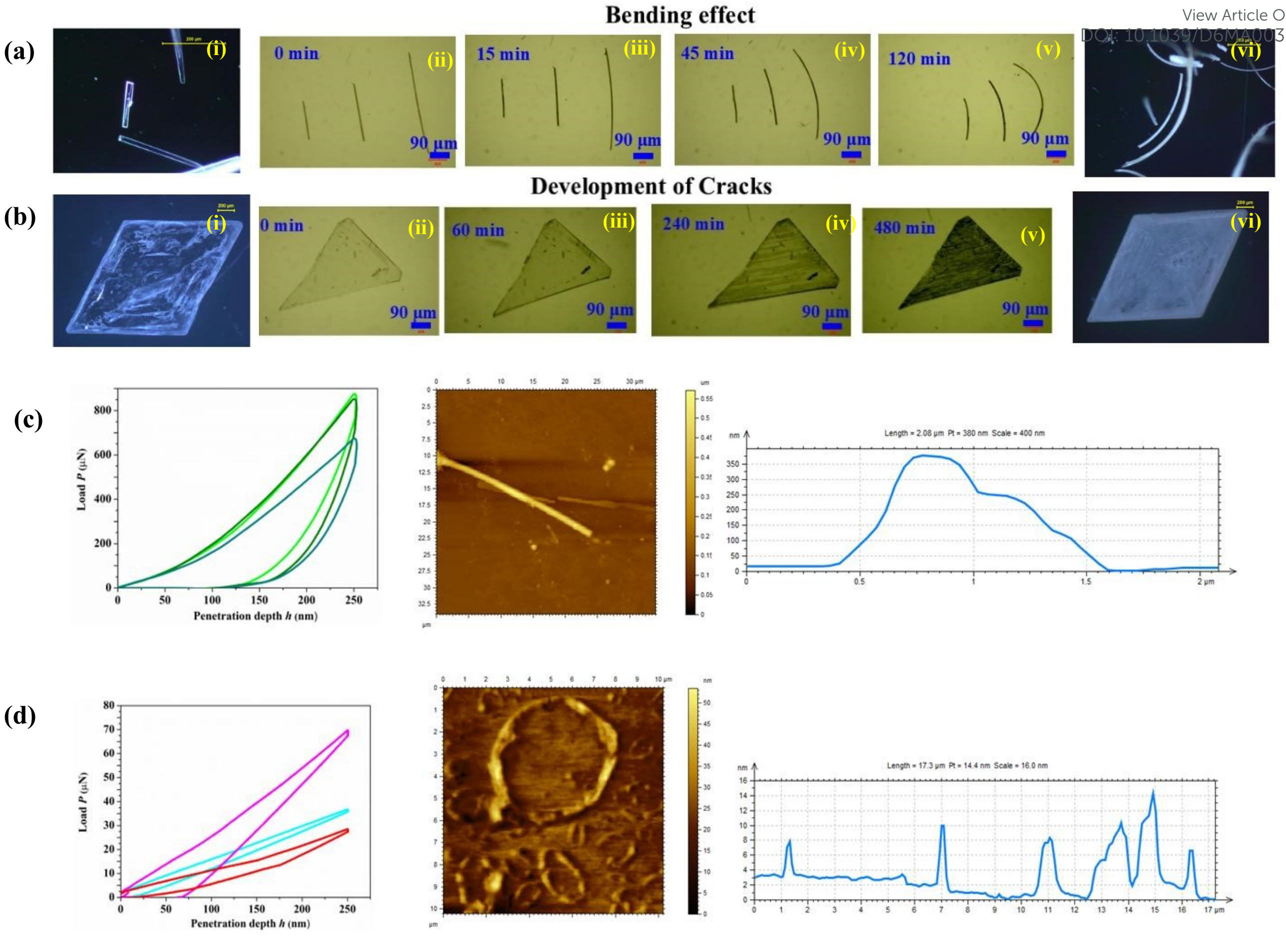

Figure 3. Optical microscope images illustrating bending (a(i-vi)) in single crystals of $B_2(A_{24})_2$ and (b(i-vi)) development of cracks in $B_3(A_{24})_2$crystals, (i) and (vi) are dark field images before and after the irradiation in both cases. *P-h* curve for $B_2(A_{24})_2$ (c) before and (d) after irradiations. AFM images for $B_2(A_{24})_2$ (e) before and (f) after irradiation; from left to right: 2D AFM and 3D AFM height profile

Crystal softness is linked to photoresponsive mechanical behaviour. Stiffness (Young's modulus, *E*) and hardness (*H*) are quantified from nanoindentation load-depth (*P-h*) curves. (Figure 3c,d, S18; ESI). The surface mechanical properties of $B_2(A_{24})_2$ and $B_3(A_{24})_2$ correlate well with their bulk mechanical characteristics before and after irradiation. For irradiated $B_2(A_{24})_2$, a displacement of 250 nm occurred under a modest load of 67.5 µN, whereas achieving the same displacement in the non-irradiated sample required a much greater load of 776 µN. The reduction in hardness (*H*: from 0.4749± 0.1723 GPa to 0.0959± 0 0858 GPa) and Young's modulus (*E*: from 9.50± 1.99 GPa to 1.55± 0.7305 GPa) indicates more softness following dimerization accompanied bending. The hardness (*H*) is comparable to the frequently reported organic crystals in the literature that undergo elastic or elasto-plastic bending upon photodimerization (Table S5). In comparison, $B_3(A_{24})_2$ crystals are substantially stiffer, requiring a force of 6.428 mN to achieve a 250 nm indent. After irradiation, these crystals become more fragile, with only 4.834 mN needed for the same displacement. The corresponding drop in hardness (*H*: from 4.18± 1.06 GPa to 4.09± 0.3039 GPa) and modulus (*E*: from 56.83± 2.96 GPa to 55.25± 3.09 GPa) further reflects the decline in mechanical robustness post-irradiation.

Although the crystals were intact after photoirradiation, they were found to be opaque and non-diffracting by single-crystal X-ray diffraction. The PXRD patterns of the irradiated material are found significantly altered from the parent crystals (Figure S2; ESI). Good quality single crystals of ethylene diamine salts of of HH-*rctt*-cpcb dimers namely *d*- $B_2(A_{24})_2$ and *d*- $B_2(A_{34})_2$ were recrystallised from DMSO-acetone (1:3, v/v) and MeOH-nitrobenzene (3:0.5, v/v) mixture respectively. Crystal structure analysis shows formation of head-to-head dimer in both cases, as evident of ^{1}H NMR spectra (Figure 4). The crystals structures of both are found to be isostructural and crystallise in $P2_1/c$ space group. The asymmetric units contain one full unit of ethylenediamine cation with HH-*rctt*-2,4/3,4-cpcb dimer. Two carboxylates of HH-*rctt*-2,4/3,4-cpcb dimer form seven N-H···O hydrogen bonds with ethylenediammonium cation (N···O: 2.745(4) Å-3.300(4) Å; <N-H···O: 112°-174°). Such type of hydrogen-bonding pack to form a bilayer structure of alternating hydrophilic and hydrophobic layers, similarly as

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$B_2(A_{24})_2$ monomer (Figure S19; ESI). C–C bond length of 1.582 Å (in case of $B_2(A_{24})_2$) and 1.575 Å $B_2(A_{34})_2$ confirms the formation of cyclobutane rings. Moreover, solid state photoluminescence (PL) spectra of the salts after photoirradiation showed greatly quenched luminescence emission profiles from before, mainly due to loss of conjugation on dimerization (Figure S20; ESI).

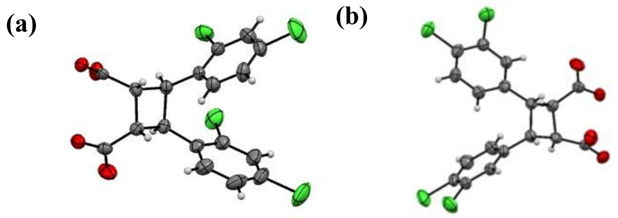

Figure 4. ORTEP drawing of the head-to-head dimer of (a) $B_2(A_{24})_2$, (b) $B_2(A_{34})_2$.

Leveraging the abundant N^+-H···O^- hydrogen bonding interaction and high propensity of iodine to engage in intra/inter halogen bonding interaction (-Cl···I, -N···I, -O···I), we explore the ability of the salt's to absorb iodine vapour. To conduct the investigation, a vial containing 20 mg of as-synthesised salts were placed into the sealed container containing solid iodine beads. The sealed container was heated at 70 °C for 5 hours to ensure complete volatilization of iodine. To monitor the uptake kinetics, samples were removed every 1-hour intervals, allowed to cool to room temperature, and weighted. These experiments were repeated on three different batches of salt samples and found that the results are consistent. After adsorption of I_2 by the B_2 salts, the sample turned sticky and adhered strongly to the container, making it difficult to remove. Various analyses including visual colour changes, TGA, and X-ray photoelectron spectroscopy confirmed effective iodine uptake by the B_3 and B_4 salts (Figure 5a, S21 & S22; ESI). The highest amount of iodine loading of was found to be 330 mg g^{-1} for $B_3(A_{24})_2$ salt (Figure 5b). $I_2@B_3(A_{24})_2$ and $I_2@B_4(A_{34})_2$ contain ~0.7 and ~0.2 molecules of I_2 per salt molecule respectively whereas, $I_2@B_4(A_{24})_2$ and $I_2@B_4(A_{34})_2$ absorb ~0.3 and ~0.1 molecules of I_2 per salt molecule, respectively. I_2 uptake values are comparable to the frequently reported adsorption values of porous organic polymers (POPs) and MOFs (Table S6). TGA revealed that pristine $B_3(A_{24})_2$ is stable up to ≈365 °C, whereas I_2 absorbed materials ($I_2@B_3(A_{24})_2$) is stable up to ≈330 °C. The TGA of $I_2@B_3(A_{24})_2$ displayed an initial weight loss of 14.07% at ≈157 °C, corresponding to the adsorbed iodine. Similarly, the TGA of $B_4(A_{24})_2$ and $I_2@B_4(A_{24})_2$ indicates that they are stable up to ≈335 °C and ≈238 °C respectively. $I_2@B_4(A_{24})_2$ undergoes 12 % weight loss at ≈125 °C due to release of adsorbed iodine (Figure S21; ESI).

The FESEM images of $I_2@B_3(A_{24})_2$ revealed no significant change in surface morphology except adhered iodine crystals to the surface (Figure S23; ESI). The elemental mapping and energy dispersive X-ray spectroscopy (EDX) analysis confirmed the homogenous distribution of iodine along with the C, N, O and Cl within the $I_2@B_3(A_{24})_2$ (Figure S23; ESI). FT-IR spectrum of the salts before and after I_2 adsorption were compared; the spectra were nearly superimposable (Figure S24; ESI), suggesting weak interactions of I_2 with salts.

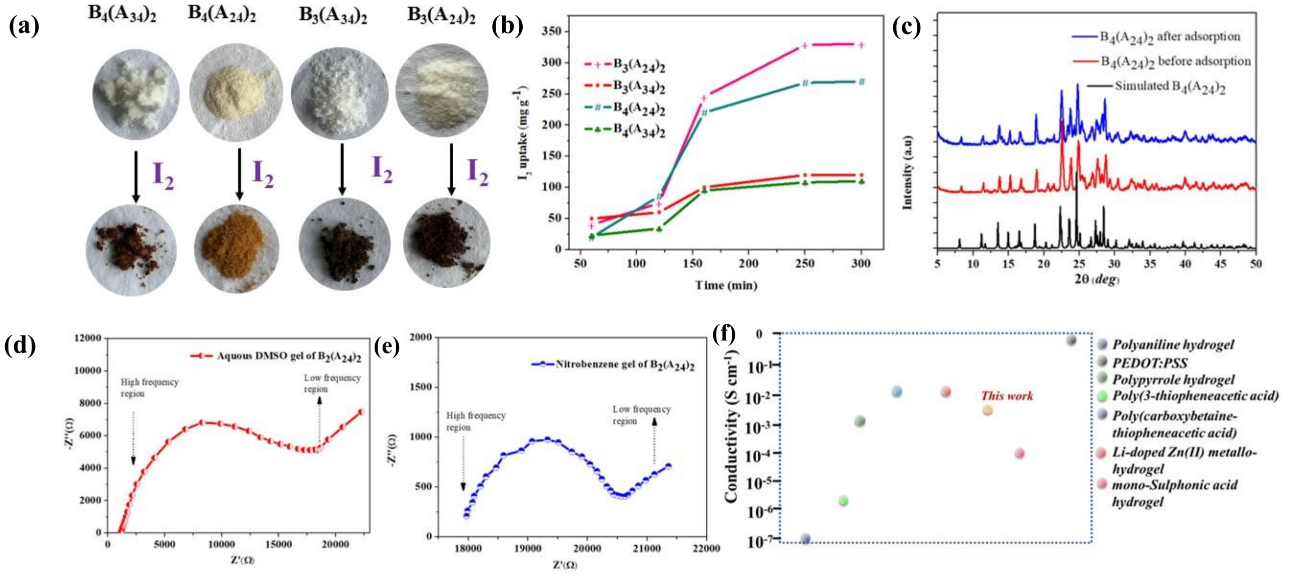

Figure 5. (a) Photographs of the salts before and after exposure to iodine; (b) iodine uptake in B_3 and B_4 salts as a function of time. note that the $B_3(A_{34})_2$ and $B_4(A_{34})_2$ plots overlay almost exactly. (d) PXRD data showing no change after iodine adsorption in $B_4(A_{24})_2$; similar observation was shown for all the other cases (Figure S25, ESI); Nyquist impedance plots of the (e) aqueous-DMSO gel (f) nitrobenzene gel of $B_2(A_{24})_2$. (g) Comparison of conductivity of different hydrogel.

PXRD patterns of as synthesized salts before and after I_2 adsorption were in good agreement, indicating no phase change due to I_2 adsorption which further supported physical adsorption of I_2 through weak interactions (Figure 5c, S25; ESI). Raman spectra revealed consistent peak around 109 cm^{-1} in all I_2 adsorbed B_3 and B_4 salts, due to symmetric stretching of perturbed I_3^- ions, and the symmetric stretching of perturbed I_2 appears around 168 cm^{-1} (Figure S26; ESI).

Previous studies on carboxylates salts have demonstrated high electrical conductivity owing to N^+-H···O^- hydrogen bonding interaction.[40] Encouraged by this and by the presence immobilized solvents (DMSO, H_2O) within gel matrix, we performed electrochemical impedance spectroscopy (EIS) measurements to explore the conductance properties of organogel. The development of highly electrically conductive materials is essential for advancing next-generation technologies such as electrochemical sensing, fuel cells, and flexible electronic devices.[54] Aqueous-DMSO gels are advanced conductive materials designed particularly for applications requiring high electrical conductivity and anti-freezing properties.[55] The fact that the OGs was able to lit LED bulb when connected through copper electrodes in a home-made electrical circuit powered by a battery confirmed their ability to conduct electricity (Figure S27; ESI). Nyquist plots show a semicircle in the high frequency region followed by a linear evolution in the low frequency region. The conductivity value was calculated to be 5.2×10^{-3} S cm^{-1} and 3.4×10^{-4} S cm^{-1} at 25 ^{0}C from the equation $\sigma = d/(R_b \times A)$, where R_b, d and A are the bulk resistance, thickness and area for the $B_2(A_{24})_2$ aqueous-DMSO and nitrobenzene gel, respectively (Figure 5d,e & S28a; ESI). Electrical conductivity cannot be measured effectively with pure water-DMSO solution because of the absence of sufficient free, mobile ions. According to current literature, the conductivity values are comparable with few polymeric and metallo-supramolecular hydrogel (Figure 5f, *ref*. S6-S11). It may be noted that during the measurements, no degradation of the hydrogel was observed. Measuring the conductivity of the xerogels in the pelleted structure proved ineffective as they are essentially non-conducting at 100 μA current flow because dehydration eliminates their primary charge carriers.[56] The conductivities of the iodine-loaded xerogel pellets at 25 ^{0}C are calculated to be in the range of 10^{-5}-10^{-6} S cm^{-1}(Figure S28b,c).

Conclusions

In conclusion, we have successfully developed a series of new organic materials; alkyl diamine ($B_{2\text{-}4}$) salts of 2,4/3,4- dichloro cinnamic acid (A_{24} or A_{34}). By leveraging the chloro-substitution strategy to direct β-type packing, we have demonstrated efficient [2+2] photodimerization in single crystals, as-synthesized materials and organogels. The crystals of $B_2(A_{24})_2$ and $B_3(A_{24})_2$ showed striking [2+2] dimerization mediated photomechanical responses including bending, development of cracks and surface peeling. Nanoindentation and AFM analyses quantified this behavior, revealing a significant reduction in Young's modulus and hardness after irradiation, consistent with macroscopic crystal "softening." Four of the six salt combinations formed stable, thermo-reversible organogels. These gels showed [2+2] photoreactivity comparable to their crystalline or as-synthesised counterparts, representing first examples of their kind. The B_3 and B_4 salts exhibited reasonable iodine capture capacity (up to 330 mg g^{-1}), owing to weak interactions with the -Cl functionality. These materials can be potential platforms for iodine remediation. Further, organogels showed good electrical conductivity (5.2×10^{-3} S cm^{-1}) at room temperature. This positions these 'salt-gels' as promising candidates for flexible electronics and conductive sensors.

Conflicts of interest

There are no conflicts to declare.

Data availability

The supporting information of this study's findings are included in the article and ESI.

Author contributions

All authors have given approval to the final version of the manuscript.

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Data availability

The supporting information of this study's findings are included in the article and ESI.