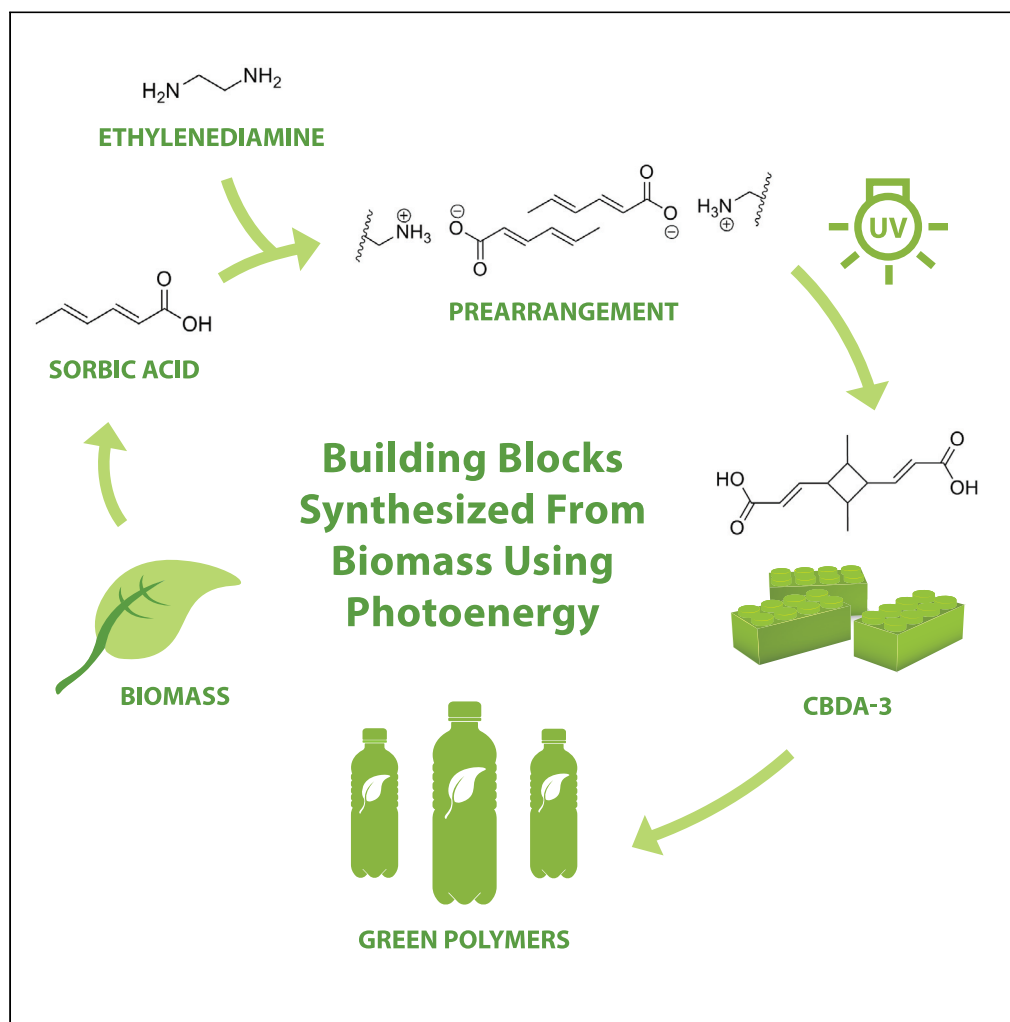


Article

A biorenewable cyclobutane-containing building block synthesized from sorbic acid using photoenergy



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Highlights

A novel cyclobutane-containing diacid building block

A potentially sustainable alternative to petroleum-derived diacids

Photoreaction using ECO-UV (Energy-efficient, Cost-effective, and Operator-friendly)

Article

A biorenewable cyclobutane-containing building block synthesized from sorbic acid using photoenergy

Micah Mabin,¹ Quintin Elliott,¹ Zhihan Wang,¹ Angel Ugrinov,² and Qianli R. Chu^{1,3,*}

SUMMARY

A novel cyclobutane-containing diacid building block, CBDA-3, was synthesized from sorbic acid using clean, efficient [2 + 2] photocycloaddition. This photoreaction can be performed using commercially available germicidal lamps, which represent a form of ECO-UV. SC-XRD showed that the cyclobutane ring in CBDA-3 has a unique semi-rigid character, unlike more rigid aromatic rings or more flexible types of aliphatic rings. C=C bonds present in the structure of CBDA-3 provide opportunities for derivatization which could be used to alter the characteristics of polymers made from this monomer. Additionally, TGA and DSC analysis showed CBDA-3 to have excellent thermal stability. These characteristics make CBDA-3 a promising building block with the potential to be used as a sustainable alternative to traditional petroleum-derived diacids. Finally, a facile and reliable Fischer esterification of CBDA-3 was performed to tune its melting point and solubility for different applications and to demonstrate the applicability of this building block in polymer synthesis.

INTRODUCTION

Diacid building blocks are important chemical starting materials used in a wide range of applications,^(Cornils and Lappe, 2014; Stock and Biswas, 2012) the most significant of which being polymers.^(East, 2002; Edlund and Albertsson, 2003; Fakirov, 2002; Ma and Webster, 2015) One classic diacid building block, terephthalic acid, is used to make over 50 million tons of polyethylene terephthalate (PET) annually. This plastic is familiar to most people through its use in disposable plastic water bottles.^(East, 2002; Fakirov, 2002) Another common diacid building block, adipic acid, is used to make Nylon 66.^(Cornils and Lappe, 2014; Palmer, 2002) Unfortunately, most diacid building blocks currently in production, including terephthalic acid and adipic acid [\(Figure 1\)](#), and in fact most industrial chemicals currently in use, are derived from petroleum.^(Annual Energy Outlook 2014, 2014, 2014) With ever-growing concerns over the environmental impact of the use of petroleum products, and over the future availability of fossil fuels, it is becoming more and more important to find sustainable alternatives to these chemicals.^(Coates and Hillmyer, 2009; Kovash et al., 2014; Lligadas et al., 2013; Rajendran et al., 2015; Tschan et al., 2012; Wang et al., 2015a, 2015b)

To work toward a solution to this problem, our research group has recently been synthesizing a series of cyclobutane-containing diacid building blocks (CBDAs) made from biomass-derived starting materials [\(Figure 1\)](#).^(Amjaour et al., 2019; Reagen et al., 2021; Shahni et al., 2020, 2021; Wang et al., 2017, 2018, 2020, 2022) Recent examples include CBDA-1 and CBDA-4,^(Amjaour et al., 2019; Shahni et al., 2020; Wang et al., 2017, 2022) both derived from cinnamic acid, and CBDA-2,^(Reagen et al., 2021; Shahni et al., 2021; Wang et al., 2018, 2020) derived from 2-furanacrylic acid. Both of these starting acids can be readily obtained from various biomass sources such as DDGS (Dried Distillers Grains with Solubles), corn cobs, wheat bran, sawdust, or sugarcane bagasse.^(Bender et al., 2018; Bozell and Petersen, 2010; Werpy and Petersen, 2004) Ultraviolet (UV) light is then used to drive a [2 + 2] photocycloaddition reaction between C=C bonds in the starting acids, which dimerizes them, forming a cyclobutane ring and creating the diacid building block.^(Randazzo et al., 2016; Schmidt, 1971) By its very nature, the light used in these reactions is renewable, non-toxic, and produces fewer waste products than chemical reactants or catalysts.^(Albini and Fagnoni, 2004; Randazzo et al., 2016) This method of synthesis makes CBDAs a promising green alternative to traditional petroleum-derived diacid building blocks. Recently, it has been shown

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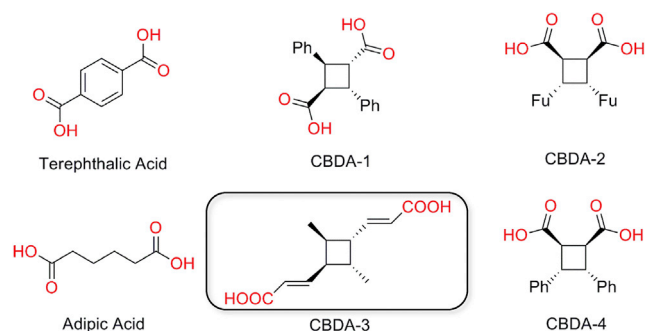


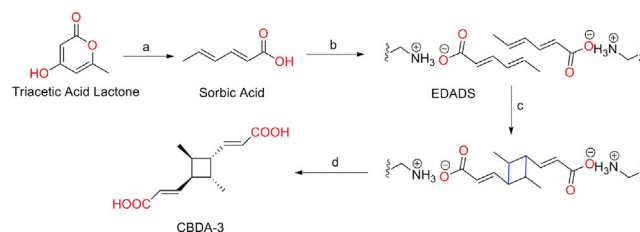
Figure 1. Examples of diacid building blocks, including terephthalic acid, adipic acid, and some CBDAs
The box highlights the focus of this work.

that CBDAs can be used to produce both thermoplastics and thermosets with excellent properties. (Amjaour et al., 2019; Shahni et al., 2020; Wang et al., 2017, 2018, 2020, 2022)

Herein we report the dimerization of biomass-derived sorbic acid to form the novel building block CBDA-3 (Scheme 1). Sorbic acid can be readily derived from triacetic acid lactone, which has the potential to be a platform chemical for the production of commercially valuable chemical products (Chia et al., 2012; Shanks and Keeling, 2017) or novel materials. (Hou et al., 2014a; Zheng et al., 2008) CBDA-3 shares the advantages of renewability and green synthesis with other CBDAs, while also having some unique properties of its own which make it an attractive building block for use in polymer synthesis. Additionally, by polymerizing CBDA-3 with another bio-based chemical such as glycerol, it would be possible to synthesize a 100% biomass-derived polymer. (Wang et al., 2018, 2020, 2022) A simple and reliable esterification reaction was used to demonstrate the usefulness of CBDA-3 in this regard.

RESULTS AND DISCUSSION

The synthesis of CBDA-3 starts with sorbic acid. However, unlike the starting materials used in the synthesis of previous CBDAs, sorbic acid gave multiple products besides some unidentified polymer(s) and unreacted starting material when exposed to UV light. (Green et al., 1971) This is presumably because the C=C bonds in the closest neighboring molecules may react in different ways due to the packing of sorbic acid in the crystalline solid. Moreover, the C=C bonds in the sorbic acid crystals are offset by more than 2.4 Å from their reaction partners, leading to poor π orbital overlap, which is critical for the success of the locally confined photoreaction. (Wang et al., 2015a) Thus, it was necessary to alter its structure using crystal engineering. (Biradha and Santra, 2013; d'Agostino et al., 2016; Kole et al., 2015; Matsumoto, 2005; Matsumoto et al., 2000; Tsaggeos et al., 2012) According to Schmidt's topochemical principles, in order for two C=C bonds to react via [2 + 2] photocycloaddition in the solid state, they need to be parallel and less than 4.2 Å apart. (Schmidt, 1971) To this end, a 2:1 salt of sorbic acid and ethylenediamine was prepared by growing crystals from an ethanol solution (Figure 2). (Ito, 1998; Ito et al., 1995) In this salt (ethylenediaminium disorbate or EDADS), hydrogen bonds and electrostatic interactions between ethylenediamine and sorbic acid arrange the sorbic acid molecules in a way that their tail-end C=C bonds are parallel



Scheme 1. Synthesis of CBDA-3 from sorbic acid

- Sorbic acid can be obtained from the biorenewable molecule triacetic acid lactone.
- Ethylenediamine forms the salt EDADS with sorbic acid.
- UV light dimerizes sorbic acid molecules by [2 + 2] photocycloaddition.
- Ethylenediamine is removed to give CBDA-3.

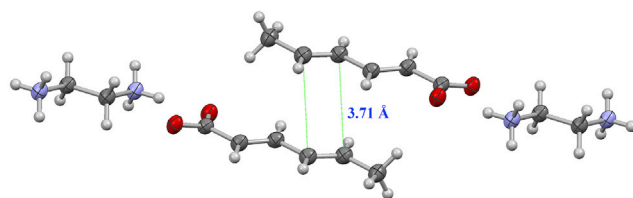


Figure 2. X-ray single crystal structure of ethylenediamine disorbate (EDADS) in Oak Ridge Thermal Ellipsoid Plot (ORTEP) representing 50% electron density

The tail end C=C bonds of two sorbic acid molecules are parallel and separated by 3.71 Å. (Sorbic acid and ethylenediamine are in a 2:1 ratio, but two ethylenediamine molecules are shown here for clarity in discussion.)

and separated by 3.71 Å, satisfying the Schmidt Principles. Furthermore, the C=C bonds in the closest neighboring molecules are offset by only about 0.7 Å, setting the stage for the corresponding [2 + 2] photocycloaddition. This structure was confirmed by single crystal X-ray diffraction (SC-XRD). The EDADS crystals were then ground to a powder and scattered on a quartz plate which was exposed to UV light from a 450-watt medium-pressure mercury arc lamp. The progress of the [2 + 2] photocycloaddition was monitored using $^1\text{H-NMR}$ and FT-IR, which showed that the reaction was complete after 19 days (Figure 3). The $^1\text{H-NMR}$ spectrum showed the disappearance of two peaks corresponding to the reaction of the tail-end C=C bond of sorbic acid (6.07 and 6.18 ppm), and the appearance of two new peaks corresponding to the formation of the cyclobutane ring (2.57 and 2.77 ppm). The peak from the methyl group of sorbic acid also shifted upfield from 1.73 to 0.98 ppm due to deconjugation. After UV irradiation, the powder was collected and dissolved in water, which was then added to a separatory funnel and acidified with hydrochloric acid. The CBDA-3 was then separated from the ethylenediamine by extracting it with ethyl acetate. During this step, the ethylenediamine can be collected for reuse if desired. The crude CBDA-3 was purified using column chromatography to give the pure product as a white powder with an isolated yield of 40%. Besides $^1\text{H-NMR}$ and FT-IR, CBDA-3 was further characterized using $^{13}\text{C-NMR}$, DEPT135, DEPT90, COSY, HRMS, and UV-Vis (See Figures S1–S6 in the ESI).

During the course of the experiments, it was found that several of the steps could be optimized in various ways to make the synthesis more efficient. First, it was found that EDADS could be prepared simply by grinding a 2:1 ratio of sorbic acid and ethylenediamine together in a mortar and pestle, rather than growing crystals from an ethanol solution. (James and Friščić, 2013) This method is much faster, taking only minutes compared to the days it takes for crystals to grow. It also produces no waste products as no solvents are

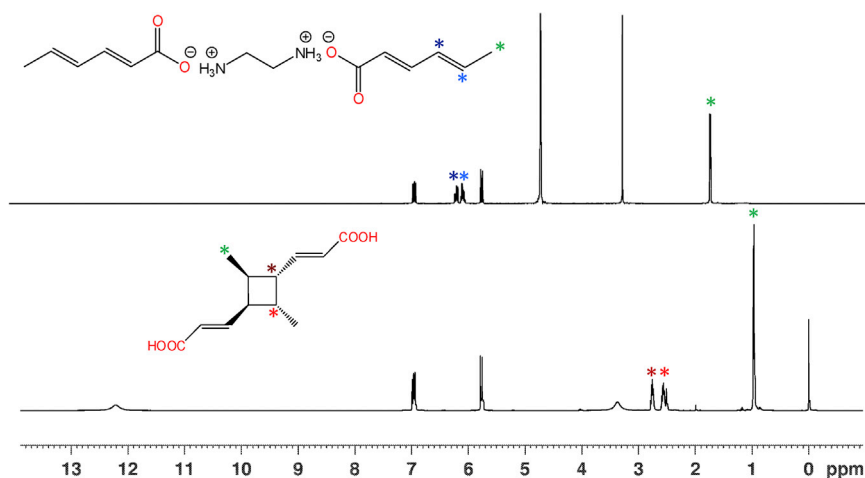


Figure 3. $^1\text{H-NMR}$ spectra of EDADS (top, D_2O) and CBDA-3 (bottom, DMSO-d_6), showing the disappearance of two peaks at 6.07 and 6.18 ppm, corresponding to the tail-end C=C bond of sorbic acid (navy and blue stars) and the appearance of peaks at 2.57 and 2.77 ppm, corresponding to the formation of the cyclobutane ring in CBDA-3 (ruby and red stars)

Also apparent is the upfield shift of the methyl peak from 1.73 to 0.98 ppm, owing to the loss of the adjacent C=C bond (green stars).

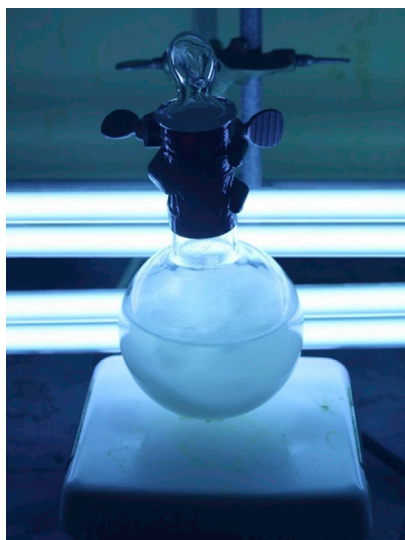


Figure 4. An example of a reaction utilizing germicidal lamps and slurry conditions

5 g of EDADS is suspended in hexane by stirring vigorously in a quartz flask, which is placed between four 95-watt germicidal lamps. (In this image the front two lamps have been removed for clarity).

involved. FT-IR showed that the spectrum of the EDADS obtained using mechano-chemical grinding in the mortar and pestle was identical to that of the EDADS obtained by crystallization (See [Figure S3](#) in the ESI).

Secondly, it was found that the [2 + 2] photocycloaddition could be achieved using commercially available germicidal lamps ([Figure 4](#)), rather than the more traditional medium-pressure mercury arc lamp photo-reactor. It was found that these germicidal lamps produce similar results yet use just a fraction of the power (3-20%) of the more traditional lamps. This is likely because the emission spectra of these low-power lamps consist of narrower bands, i.e., more of the energy is concentrated in wavelengths that produce the target reaction, rather than being wasted in extraneous wavelengths and heat. These lamps are also much less expensive, costing just 1-6% as much as medium-pressure lamps. They also are generally simpler and easier to use, as many are designed for use by non-chemists, which has the added benefit of making them safer as well. As such, these germicidal lamps are an example of ECO-UV. ECO-UV is an acronym for energy-efficient, cost-effective, and operator-friendly UV.

Thirdly, it was found that ethylenediamine (b.p.: 116°C) slowly evaporated from the organic salt (EDADS) when exposed to UVC light, presumably due to the heat from the UV lamps and the change in the crystal lattice with the formation of CBDA-3. To inhibit the evaporation of ethylenediamine, EDADS was sealed between two quartz plates for photoreaction. The isolated yield was improved from 40% to 51%.

Lastly, it was of interest to scale up the [2 + 2] photocycloaddition step. The solid-state reaction worked well for amounts of EDADS up to about 1 g, but since the powder needs to be spread in a thin layer on a quartz plate, the size of the plate required would become prohibitively large for larger amounts of EDADS. Doing a solution-phase photoreaction of EDADS was not an option as its crystal structure is important to the formation of CBDA-3 and must be preserved during UV irradiation. Instead, a slurry of EDADS in hexane, which is a poor solvent of EDADS, was prepared ([Figure 4](#)). The particles were kept suspended in the hexane by vigorous stirring. This also helped to expose much more surface area to the UV than would be possible in a solid-state reaction of a similar scale. Using this method, photoirradiation of a 5 g sample of EDADS was completed in 14 days. The workup of this sample gave the product CBDA-3 in 57% isolated yield.

Crystals of CBDA-3 were grown in both methanol and a 1:1 mixture of hexane and ethyl acetate, and its single crystal structure was reported for the first time ([Figure 5](#) and ESI). One feature of CBDA-3 apparent in the single crystal structure is the puckered conformation adopted by the cyclobutane ring. (Brown et al., 2013; FrancisCarey, 2007; Rappoport and Liebman, 2005) The ring is not flat; rather, it has a torsion angle of 18.5°. This means that the cyclobutane ring is not completely rigid like a planar aromatic ring, nor is it completely flexible like a typical aliphatic ring. It has a unique, semi-rigid quality that is intermediate to the two, which may be a useful property that can be exploited in a variety of polymer applications. For example, using a CBDA to partially replace aromatic diacid building blocks of polymers could increase

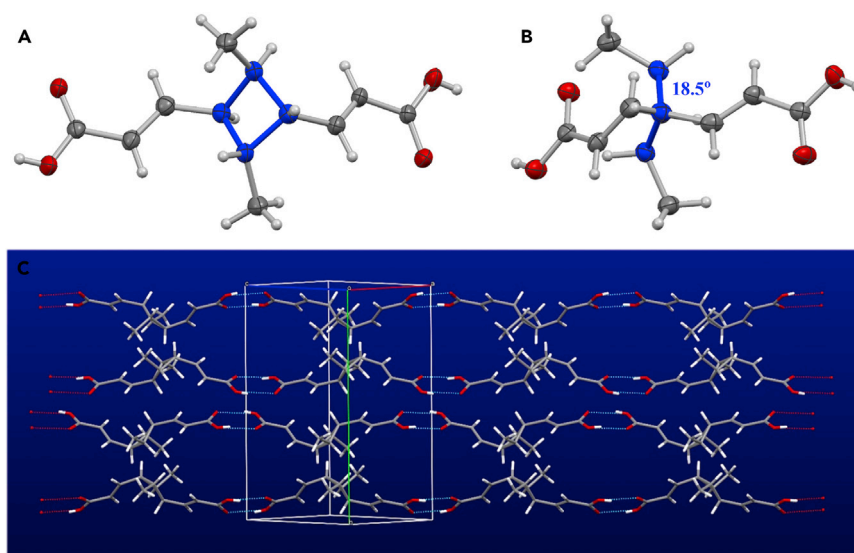


Figure 5. The X-ray single crystal structure of CBDA-3

(A and B) Two views of the crystal structure in Oak Ridge Thermal Ellipsoid Plot (ORTEP) representing 50% electron density (except for hydrogen atoms). The cyclobutane ring is highlighted in blue with the 18.5° torsion angle apparent in the second image.

(C) Side view of four crystal unit cells showing the 1D linear network of hydrogen bonds between the molecules and packing of the molecules.

their solubility and processibility without significantly compromising their desired mechanical properties. Another feature of CBDA-3 that can be seen in its crystal structure is the presence of its two unreacted C=C bonds (Atkinson et al., 2011; Weathersby et al., 2018) which is a unique feature of CBDA-3 compared to previous CBDAs. These C=C bonds are reactive functional groups that could be exploited to fine-tune the properties of the polymers made from CBDA-3 by reacting them with various reagents to create derivatives (e.g., epoxides) (Liu et al., 2021; Ma et al., 2016). These C=C bonds may also be useful in making cross-linked polymers with CBDA-3 through radical polymerization or additional [2 + 2] cycloaddition reactions. Last but not least, a one-dimensional (1D) linear network of hydrogen bonds ($O_{C=O} \cdots O_{OH} = 2.62 - 2.67 \text{ \AA}$, Figure 5C and ESI) in the crystal of CBDA-3 shows its potential in preparing supramolecular materials like hydrogen-bonded organic frameworks (HOFs) (Hou et al., 2014b; Wang et al., 2014) and green metal-organic materials (GMOMs) (Chu et al., 2018; Shahni et al., 2021; Stock and Biswas, 2012).

As few materials with industrial applications contain the cyclobutane moiety, Making a lasting impression: Tritan™ copolyester http://www.eastman.com/Brands/Eastman_Tritan/ (Accessed in Aug 2022), there may be concerns over its stability in polymer applications due to its high ring strain energy, which is about 20.1 and 26.2 kcal/mol higher than that of cyclopentane or cyclohexane, respectively. (Anslyn and Dougherty,

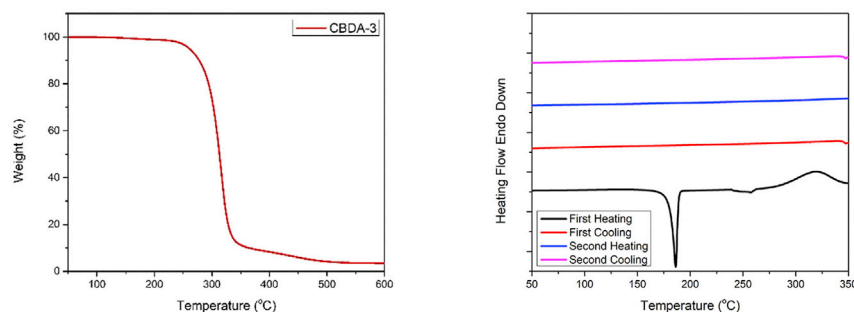
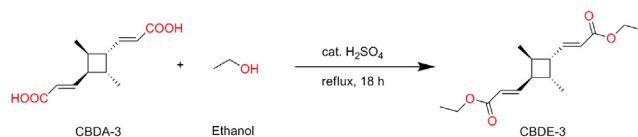


Figure 6. TGA (left) and DSC (right) curves of CBDA-3

TGA was recorded from 50°C to 600°C with a heating rate of 20°C/min under N_2 atmosphere. DSC was recorded from 50°C to 350°C with a heating rate of 10°C/min under N_2 atmosphere.



Scheme 2. Synthesis of CBDE-3 via Fischer esterification of CBDA-3 and ethanol

2006) Nevertheless, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed that CBDA-3 is highly thermally stable up to at least 250°C (Figure 6), with 5% weight loss at 285°C ($T_{d5\%}$) and 50% weight loss at 313°C, which is sufficiently stable for use as a building block in most applications. This stability is presumably because [2 + 2] cycloaddition and its reverse ring-opening process is generally thermally forbidden according to Woodward-Hoffmann rules, (Hoffmann and Woodward, 1965) meaning that the cyclobutane ring is difficult to break using thermal energy once it is formed by photoreaction. Additionally, the melting point of CBDA-3 was measured at 178-179°C.

To highlight the potential application of CBDA-3, Fischer esterification was performed by stirring a solution of CBDA-3 in ethanol, with a small amount of sulfuric acid added as the catalyst, at reflux for 18 h (Scheme 2). From this reaction, the cyclobutane-containing diester, CBDE-3, was obtained as a pale yellow liquid with a 91% yield. As a liquid, this ester can be more easily utilized in solvent-free polymerization. (Ball-Jones et al., 2016; Hosoi et al., 2017; Liu et al., 2021) Additionally, CBDE-3 was found to be more soluble than CBDA-3 in most of the common and/or green solvents such as acetone, ethanol, and MeTHF, as was expected. As most organic reactions are performed in organic solvents, this is a highly useful property. Also demonstrated by this esterification reaction is the readiness of CBDA-3 to undergo condensation reactions with alcohols, which may be exploited in polymer synthesis. For instance, if the ethanol used in this reaction were to be replaced with a diol or triol, linear or cross-linked polymers of CBDA-3 could be obtained, respectively. Similar polymerization has been successfully carried out using CBDA-1 and CBDA-2 in our previous works. Many such alcohols, such as ethylene glycol and glycerol, can also be derived from biomass sources, resulting in a method that is able to create 100% bio-based polymers.

Conclusions

A novel building block, CBDA-3, was introduced to materials synthesis. Sorbic acid, which can be obtained from the biomass-derived molecule triacetic acid lactone, was prearranged into the photoreactive conformation by combining with ethylenediamine to form a salt. Upon exposure of this salt to UV light, CBDA-3 was then formed via a [2 + 2] photocycloaddition reaction. Subsequent removal of the ethylenediamine yielded the product CBDA-3 which was then analyzed using SC-XRD. Evident in its crystal structure were the semi-rigid nature of the cyclobutane ring and the derivatization potential of its C=C bonds, which are favorable qualities that may be useful in a wide range of green polymer applications. Additionally, CBDA-3 was shown by TGA and DSC to have excellent thermal stability. The synthesis of CBDA-3 was optimized in a number of ways during the experiments. These optimized procedures, including the use of mechano-chemical grinding, ECO-UV lamps, and slurry reactions, may be useful to researchers in making a wide variety of synthesis reactions more efficient. Furthermore, an ester of CBDA-3 and ethanol was prepared by simple and reliable Fischer esterification, highlighting the potential applicability of this building block. Due to their structural similarities, CBDA-3 and other CBDAs could be used as sustainable alternatives to commodity petrochemicals widely used in polymers, such as terephthalic acid and adipic acid.

Limitations of the study

Compared with the synthesis of our previous CBDAs, this topochemical photoreaction only afforded medium yield, and reaction time was long. Meanwhile, it was challenging to recover pure ethylenediamine on a small scale mainly due to its relatively low boiling point (i.e., 116°C), so it was recovered as its HCl salt form.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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 - Synthesis of CBDA-3
 - Synthesis of CBDE-3 (Fischer esterification)
 - Crystallization

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2022.105020>.

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AUTHOR CONTRIBUTIONS

M. M. carried out the experiments and prepared the first draft of the article as well as edited the article. Q. E. suggested the use of germicidal lamps as an inexpensive and green irradiation source of the photoreactions. Z. W. helped to perform the experiments. A. U. collected, solved, and refined the X-ray single crystal structures. Q. R. C. conceived the concept, directed the project, and revised the article.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
sorbic acid	Alfa Aesar	Cas: 110-44-1
ethylenediamine	Alfa Aesar	Cas: 107-15-3
hexane	Thermo Fisher Scientific	Cas: 110-54-3
methanol	Thermo Fisher Scientific	Cas: 67-56-1
ethanol	Thermo Fisher Scientific	Cas: 64-17-5
ethyl acetate	Thermo Fisher Scientific	Cas: 141-78-6
hydrochloric acid	Thermo Fisher Scientific	Cas: 7647-01-0
sulfuric acid	Thermo Fisher Scientific	Cas: 7664-93-9
sodium bicarbonate	Thermo Fisher Scientific	Cas: 144-55-8
Software and algorithms		
ChemDraw 2010	PerkinElmer (CambridgeSoft)	https://www.perkinelmer.com/category/chemdraw
Mercury 2020.3.0	Cambridge Crystallographic Data Center (CCDC)	https://www.ccdc.cam.ac.uk/solutions/csd-core/components/mercury
Other		
Hanovia medium pressure mercury arc lamp	Ace Glass Incorporated	https://www.aceglass.com/
germicidal lamp (TUV 25W/G25 T8 and TUV PL-L 95WWHO/4P)	Philips	https://www.lighting.philips.com/main/products/uv-disinfection/uvc-lamps

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Qianli Rick Chu (chu@chem.und.edu).

Materials availability

All materials generated in this study are available in the article and [supplemental information](#) or from the [lead contact](#) without restriction upon reasonable request.

Data and code availability

All data reported in this paper will be shared by the [lead contact](#) upon request.

This paper does not report original code.

Any additional information required to reanalyze the data reported in this paper is available from the [lead contact](#) upon request.

METHOD DETAILS

General information

All reagents were purchased from Alfa Aesar and Thermo Fisher Scientific, and used without further purification. The lights sources used for the photoreactions were a Hanovia medium pressure mercury arc lamp (PC 451050, 450 W), or Philips germicidal lamps (TUV 25W/G25 T8 and TUV PL-L 95WWHO/4P). Thin-layer chromatography (TLC) was performed on silica gel W/UV 200 μm precoated plates. Column chromatography was performed using a 15 cm silica gel column and a 3:1 mixture of hexane/ethyl acetate as the mobile phase. The solution phase nuclear magnetic resonance spectra (NMR) were recorded on a Bruker AVANCE (^1H : 500 MHz; ^{13}C : 125 MHz). All spectra were obtained in deuterium dimethyl sulfoxide (DMSO- d_6) or deuterium oxide (D $_2$ O). For DMSO- d_6 or D $_2$ O solution, the chemical shifts were reported as parts per million (ppm) with tetramethylsilane as a standard. Coupling constants are reported in hertz

(Hz). Data for ^1H NMR spectra are reported as follows: chemical shift (ppm: referenced to parts per million), s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constant (Hz), and integration. Infrared spectroscopy (IR) was recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. UV/vis spectroscopy was performed using a Beckman DU-640 spectrophotometer. Single crystal X-ray data were recorded on a Bruker Kappa Apex II Duo X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$). The mass spectrometric analyses were performed using a high-resolution time-of-flight G1969A with electrospray (atmospheric pressure chemical) ionization (Agilent, Santa Clara, CA) and reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[\text{M} + \text{Na}]^+$, $[\text{M} + \text{H}]^+$, $[\text{M} + \text{NH}_4]^+$, or $[\text{M}]^+$. Melting points were measured on a Stanford Research Systems (SRS) DigiMelt MPA160 without correction at a ramp rate of $2^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was performed on TA SDT Q600 instrument with a heating rate of $20^\circ\text{C}/\text{min}$ under N_2 atmosphere. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Jade DSC at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. Photomicrographs were taken with a Zeiss Axioplan upright fluorescent microscope.

Synthesis of EDADS

Method A, crystallization: sorbic acid (10.0 g, 89.2 mmol) and ethylenediamine (3.2 mL, 47.0 mmol) were dissolved in ethanol (250 mL) in a beaker, which was then left in a fume hood to evaporate. Every 48 h, the crystals that had formed were collected by filtering from the solution. The filtrate was then replaced into the beaker with 100 mL more ethanol and put back in the fume hood. After six collections, a total of 11.5 g (91%) of the product, ethylenediaminium disorbate (EDADS) was obtained as colorless needle-shaped crystals, m.p. $157\text{--}158^\circ\text{C}$.

Method B, mechano-chemical grinding: sorbic acid (5.0 g, 44.6 mmol) and ethylenediamine (1.6 mL, 23.5 mmol) were added to a mortar and pestle and ground for 15 min. The product, EDADS (6.4 g, 99%) was obtained directly as a white powder, m.p. $157\text{--}158^\circ\text{C}$. ^1H NMR (500 MHz, D_2O): δ 6.95 (q, $J = 8$ Hz, 2H), 6.22 (t, $J = 13$ Hz, 2H), 6.06–6.13 (m, 2H), 5.77 (d, $J = 15$ Hz, 2H), 3.29 (s, 4H), 1.77 (d, $J = 5$ Hz, 6H). ^{13}C NMR (125 MHz, D_2O): δ 176.6, 142.6, 138.5, 130.0, 124.4, 37.0, 18.1. IR: 1512, 1468, 1381, 1365, 1314, 1000, 966 cm^{-1} . UV/vis: λ_{max} 252 nm.

Synthesis of CBDA-3

Method A, solid state: EDADS (1.0 g, 3.2 mmol) powder was evenly scattered on a 12.5×12.5 cm quartz plate and irradiated with a Hanovia medium pressure mercury arc lamp (PC 451050, 450 W). The progress of the reaction was monitored with FT-IR and ^1H -NMR. The reaction was found to be complete after 19 days. After the photoreaction, the powder was added to a separatory funnel with water (100 mL) and HCl (6M, 2.0 mL), and extracted with 3×50 mL ethyl acetate. Ethylenediamine was recovered from the aqueous layer as its HCl salt (388 mg, 83%). The organic layer was dried over anhydrous sodium bicarbonate and left in a fume hood to evaporate, giving crude CBDA-3 as a light brown solid. This solid was then purified by column chromatography to give the desired product, (2*E*,2'*E*)-3,3'-((1*R*,2*R*,3*S*,4*S*)-2,4-dimethylcyclobutane-1,3-diyl) diacrylic acid (CBDA-3) (320 mg, 40%), as a white powder, m.p. $178\text{--}179^\circ\text{C}$.

Method B, hexane slurry: EDADS (5.0 g, 16.2 mmol) powder was added to hexane (200 mL) in a quartz round-bottom flask and stirred vigorously to create a slurry. This flask was then placed in between 4 Philips 95W germicidal lamps (TUV PL-L 95WWHO/4P). The progress of the reaction was monitored with FT-IR and ^1H -NMR. The reaction was found to be complete after 14 days. After the photoreaction, the dried powder was added to a separatory funnel with water (500 mL) and HCl (6M, 10.0 mL) and extracted with 3×150 mL ethyl acetate. The organic layer was dried over anhydrous sodium bicarbonate and left in a fume hood to evaporate, giving crude CBDA-3 as a light brown solid. This solid was then purified by column chromatography to give the desired product, (2*E*,2'*E*)-3,3'-((1*R*,2*R*,3*S*,4*S*)-2,4-dimethylcyclobutane-1,3-diyl) diacrylic acid (CBDA-3) (2.24 g, 57%), as a white powder, m.p. $178\text{--}179^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 12.22 (s, 2H), 6.90 (q, $J = 8$ Hz, 2H), 5.78 (d, $J = 15$ Hz, 2H), 2.77 (q, $J = 8$ Hz, 2H), 2.57 (q, $J = 7$ Hz, 2H), 0.98 (d, $J = 5$ Hz, 6H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 167.4, 148.7, 122.6, 44.7, 35.4, 15.9. IR: 1690, 1632, 1413, 1308, 1314, 1210, 984 cm^{-1} . UV/vis: λ_{max} 226 nm. HRMS (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{O}_4\text{Na}$, 237.0946; found 237.0946.

Synthesis of CBDE-3 (Fischer esterification)

CBDA-3 (450 mg, 2.00 mmol), EtOH (20 mL), and H_2SO_4 (200 mg, 2.00 mmol) were added to a round bottom flask and heated to reflux for 18 h, at which point TLC showed the completion of the reaction. The EtOH was

then removed by rotary evaporator, and the remaining residue was dissolved in 200 mL hexane. This solution was washed with saturated sodium bicarbonate (100 × 2 mL), and brine (100 × 3 mL), before drying over anhydrous sodium sulfate. The hexane was then removed by rotary evaporator, giving the desired product, CBDE-3 (510 mg, 91%) as a pale yellow liquid.

Crystallization

CBDA-3 (10 mg) powder was dissolved in either methanol (15 mL) or a 1:1 mixture of hexane and ethyl acetate (15 mL) in a 20 mL vial by sonicating for 30 min. The vials were then placed uncovered in a fume hood at room temperature to evaporate and the crystals formed after three days and four days, respectively.

The crystallographic data for EDADS and CBDA-3 are available in the Cambridge Crystallographic Data Centre (CCDC# 1912650 and 1912651).