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Unexpected and divergent mechanosynthesis of furanoid-bridged fullerene dimers $C_{120}O$ and $C_{120}O_2^{\dagger}$

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An unexpected, divergent and efficient approach toward furanoid-bridged fullerene dimers $C_{120}O$ and $C_{120}O_2$ was established under different solvent-free ball-milling conditions by simply using pristine C_{60} as the starting material, water as the oxygen source and $FeCl_3$ as the mediator. The structures of $C_{120}O$ and $C_{120}O_2$ were unambiguously established by single-crystal X-ray crystallography. A plausible reaction mechanism is proposed on the basis of control experiments. Furthermore, $C_{120}O_2$ has been applied in organic solar cells as the third component and exhibits good performance.

Over the past three decades, [60]fullerene (C_{60}) and its derivatives have attracted significant attention due to their remarkable applications in numerous fields of materials science, biological applications and nanotechnology. Fullerene dimers, including C_{120} , C_{120} O and C_{120} O₂, are molecular structures linking two fullerene skeletons directly or *via* bridge(s) and are the fundamental subunits of fullerene polymers. Fullerene dimers exhibit many unique properties and thus have enormous potential for various applications.

The selective formation of the dumbbell-shaped dimer C_{120} under solvent-free and mechanical milling conditions was first disclosed in 1997 by Wang *et al.* ^{3a} Since then, more solvent-free mechanochemical methods have been reported to generate fullerene dimer C_{120} *via* different promoters, such as inorganic

mediated solution-phase synthesis of C120 was reported, providing a new approach for the synthesis of fullerene dimers (Scheme 1a).4 To date, there are few methods for synthesizing furanoid-bridged dimers C120O and C120O2, and their syntheses are generally limited by the use of preprepared fullerene derivatives as the starting material, high temperatures, long reaction times and inert atmospheres.5,6 C120O with one furan bridge was previously prepared by heating a mixture of C₆₀O and 5-6 equiv. of C₆₀ in the solid state at 200 °C for 1 h (19-20% yield)^{5a} or in 1,2-dichlorobenzene (1,2-C₆H₄Cl₂) at 180 °C for 3 days (26% yield).5b C120O2 with cages bis-linked by adjacent furanoid bridges was formed in ca. 15% yield by heating solid C₁₂₀O to 400 °C for 1 h in an argon atmosphere.6 C₆₀O was alternatively prepared by photooxygenation, a oxidation with dimethyldioxirane, he m-chloroperoxybenzoic acid, cytochrome P450 chemical models,7d methyltrioxorhenium-hydrogen peroxide^{7e} or methyl (trifluoromethyl)dioxirane^{7f} in yields ranging from 4% to 35%. Therefore, the overall yields of furanoidbridged C₁₂₀O and C₁₂₀O₂ starting from C₆₀ are estimated to be only 0.8-9% and 0.1-1%, respectively. The identities of both C₁₂₀O and C₁₂₀O₂ were deduced from their spectral data and theoretical calculations, 5,6,8 but confirmation by single-crystal Xray structures is lacking. The harsh reaction conditions and use of preprepared C₆₀O and C₁₂₀O as the starting materials in these methodologies encounter obvious limitations and prevent their practical applications. Therefore, a more straightforward and efficient approach for accessing C₁₂₀O and C₁₂₀O₂, particularly

salts, organic compounds and alkali metals.3b,c Later, the FeCl₃-

Mechanochemistry has gained increasing interest in recent years. Apart from making various chemical reactions possible under solvent-free conditions, mechanochemical reactions

from pristine C_{60} , is highly desirable.

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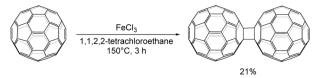
 $[\]dagger$ Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization data, NMR spectra of $C_{120}O$ and $C_{120}O_2$, X-ray crystallographic data for $C_{120}O$ and $C_{120}O_2$. CCDC 2289163, 2289161. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4sc04167d

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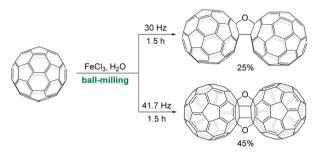
Previous work

a) Liquid-phase synthesis of C_{120} from C_{60} and $FeCl_3$



This work

b) Mechanochemical synthesis of $C_{120}O$ and $C_{120}O_2$ from C_{60} , FeCl $_3$ and H_2O



Scheme 1 Strategies for the synthesis of fullerene dimers.

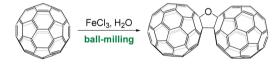
feature many unique advantages, such as shorter reaction times, cleaner and safer reaction conditions, lower energy consumption, higher product yields and even different product selectivities. 9 C $_{60}$ is barely soluble in common organic solvents, and its poor solubility somewhat restricts the exploration of its chemical reactions. Thus, mechanochemistry has emerged as an attractive alternative to conventional solution-based reactions in the field of fullerene chemistry. 10

Due to the potential application of fullerene dimers and our continuous interest in fullerene mechanochemistry, 10,11 herein we disclose the unexpected, divergent and straightforward mechanosynthesis of furanoid-bridged fullerene dimers $C_{120}O$

and $C_{120}O_2$ directly from easily available pristine C_{60} (Scheme 1b). This highly efficient mechanochemical method will provide more possibilities for practical application of these fullerene dimers and new avenues for other bridged fullerene dimers.

In attempts to mechanochemically synthesize C₁₂₀ from C₆₀ and FeCl₃, it was intriguing to discover that the addition of H₂O could alter the reaction product from C₁₂₀ to furanoid-bridged fullerene dimers. Therefore, the mechanochemical reaction of C₆₀ with FeCl₃ and H₂O was systematically investigated. The results of the reaction optimizations for the furanoid-bridged dimer C₁₂₀O are shown in Table 1. Initially, C₆₀ (0.05 mmol), 6 equiv. of FeCl₃ and 15 equiv. of H₂O were added into a stainless steel jar (5 mL) together with 4 stainless steel balls (5 mm in diameter) under solvent-free and ambient conditions and milled vigorously at 1800 cycles per minute (30 Hz) in a GT 300 mixer mill at room temperature for 90 min. The reaction mixture was dissolved in 1,2-C₆H₄Cl₂ and monitored by highperformance liquid chromatography (HPLC) on a Cosmosil Buckyprep-D column with toluene as the mobile phase. It was found that the reaction mixture consisted of the furanoidbridged dimer C₁₂₀O, dumbbell-shaped dimer C₁₂₀ and unreacted C60. The percentage of each component was calculated by quantitative analysis based on HPLC peak areas. The yield of C₁₂₀O was thus determined to be 30%, in addition to the 33% yield of C₁₂₀ (Table 1, entry 1). By increasing the amount of FeCl₃ to 7 equiv., the yield of C₁₂₀O was enhanced to 33% (Table 1, entry 2), yet further increasing the amount of FeCl₃ to 8 equiv. resulted in a substantially decreased yield of 20% due to the formation of C₁₂₀O₂ (Table 1, entry 3). In addition, no benefit to the product yield could be achieved by shortening or prolonging the reaction time (Table 1, entries 4 and 5). When the reaction was attempted in the absence of H2O, only trace amounts of C_{120} and $C_{120}O$ were detected, highlighting the pivotal role of H₂O in this mechanochemical reaction (Table 1, entry 6).

Table 1 Optimization of the reaction conditions to afford $C_{120}O^a$



Entry	Ratio ^b	Yield of $C_{120}O^c$ (%)	Yield of C ₁₂₀ ^c (%)	Recovered C ₆₀ ^c (%)
1	1:6:15	30	33	37
2	1:7:15	33	27	33
3	1:8:15	20	11	28
4^d	1:7:15	19	33	48
5^e	1:7:15	29	16	32
6	1:7:0	Trace	Trace	36
7	1:7:20	28	34	34
8	1:7:10	30	26	43
9 ^f	1:7:15	20	30	50
10^g	1:7:15	26	38	29

^a Unless otherwise noted, all reactions were performed with 0.05 mmol of C_{60} , FeCl₃, and H_2O together with 4 stainless steel balls (5 mm in diameter) in a stainless steel jar (5 mL) and milled vigorously (30 Hz) at room temperature for 90 min. ^b The molar ratio refers to C_{60} /FeCl₃/ H_2O . ^c Based on HPLC area ratios on a Cosmosil Buckyprep-D (10 × 250 mm) column. ^d The reaction time was 60 min. ^e The reaction time was 120 min. ^f The reaction frequency was 25 Hz.

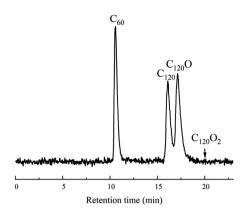


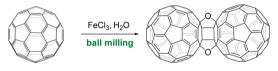
Fig. 1 HPLC chromatogram for the synthesis of $C_{120}O$ from C_{60} , H_2O and $FeCl_{\tau}$ under optimal ball-milling conditions.

Increasing or reducing the amount of $\rm H_2O$ resulted in a slightly lower yield (Table 1, entries 7 and 8 ν s. entry 2). Furthermore, the product yield of $\rm C_{120}O$ was lowered as the milling frequency was increased or decreased (Table 1, entries 9 and 10). On the basis of the results presented above and the isolated yield of $\rm C_{120}O$ for each entry, the optimized conditions to afford $\rm C_{120}O$ were determined as shown in entry 2 of Table 1: $\rm C_{60}$ (0.05 mmol), FeCl₃ (0.35 mmol), $\rm H_2O$ (0.75 mmol), a milling

frequency of 30 Hz and a milling time of 90 min. The HPLC chromatogram on a Cosmosil Buckyprep-D (10×250 mm) column with toluene as the eluent at a flow rate of 1 mL min⁻¹ and the detector wavelength at 326 nm is shown in Fig. 1. The retention times of C_{60} , C_{120} , C_{120} O and $C_{120}O_2$ were 10.6 min, 16.1 min, 17.3 min and 20.0 min, respectively. The isolated yield of $C_{120}O$ by recycling HPLC on a Cosmosil Buckyprep-D (10×250 mm) column was 25%, which was significantly higher than the 0.8–9% for the two-step procedure starting from C_{60} (*vide supra*).

During the optimization process for the synthesis of the furanoid-bridged $C_{120}O$, it was found that increasing the amount of FeCl₃ as well as the milling frequency would favour the formation of the fullerene dimer $C_{120}O_2$ with bis-linked furanoid bridges. Therefore, we further modified our reaction conditions with the expectation of obtaining $C_{120}O_2$ dominantly or even selectively. The results from HPLC analyses are summarized in Table 2. A reaction mixture of C_{60} (0.05 mmol), 9 equiv. of FeCl₃ and 15 equiv. of H_2O was milled at 2500 cycles per minute (41.7 Hz) in a GT 600 mixer mill at room temperature for 90 min. To our delight, $C_{120}O_2$ was obtained in 57% yield along with a small amount of $C_{120}O$ (7%) and a trace amount of C_{120} (Table 2, entry 1). By increasing the amount of FeCl₃ to 10 equiv., the yield was enhanced to 69% (Table 2, entry

Table 2 Optimization of the reaction conditions to afford $C_{120}O_2^a$



Entry	Additive	Ratio ^b	Yield of $C_{120}O_2^c$ (%)	Yield of $C_{120}O^{c}$ (%)	Yield of C_{120}^{c} (%)	Recovered C ₆₀ ^c (%)
1	$FeCl_3$	1:9:15	57	7	Trace	36
2^{c}	FeCl ₃	1:10:15	69	9	Trace	22
3	$FeCl_3$	1:11:15	71	Trace	Trace	26
4	$FeCl_3$	1:12:15	80	0	0	20
5^d	$FeCl_3$	1:10:15	52	10	Trace	32
6^e	$FeCl_3$	1:10:15	67	7	Trace	26
7	$FeCl_3$	1:10:0	Trace	Trace	Trace	50
8	$FeCl_3$	1:10:10	57	7	Trace	36
9	$FeCl_3$	1:10:20	63	8	Trace	29
10^f	$FeCl_3$	1:10:15	50	13	Trace	36
11 ^g	$FeCl_3$	1:10:15	60	0	0	40
12	$AlCl_3$	1:10:15	0	Trace	50	50
13	$FeCl_2$	1:10:15	0	Trace	54	45
14	$NiCl_2$	1:10:15	0	Trace	44	55
15	Oxone	1:10:15	Trace	Trace	38	42
16	m-CPBA	1:10:15	Trace	Trace	41	45
17	H_2O_2	1:10:15	Trace	Trace	39	56
18^h	$FeCl_3$	1:10:15	0	Trace	15	83
19^{i}	$FeCl_3$	1:10:15	54	17	Trace	27
20^{j}	FeCl ₃	1:10:15	15	49	16	20

 $[^]a$ Unless otherwise noted, all reactions were performed with 0.05 mmol of C_{60} , FeCl $_3$, and H_2O together with 4 stainless steel balls (5 mm in diameter) in a stainless steel jar (5 mL) and milled vigorously (41.7 Hz) at room temperature for 90 min. b The molar ratio refers to C_{60} /FeCl $_3$ / H_2O . c Based on HPLC area ratios on a Cosmosil Buckyprep (4.6 \times 250 mm) and/or Buckyprep-D (10 \times 250 mm) column. d The reaction time was 60 min. e The reaction time was 120 min. f The reaction frequency was 35 Hz. g The reaction frequency was 45 Hz. h The reaction was performed in 1,1,2,2-tetrachloroethane (0.5 mL) at 150 °C for 48 h. f Under a N_2 atmosphere. f $C_{120}O$ was used instead of C_{60} .

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2). Further increasing the amount of FeCl₃ could improve the selectivity and relative yield of C₁₂₀O₂ (Table 2, entries 3 and 4), but led to a decrease in the HPLC intensity, indicating that the amount of C120O2 was actually decreased and would lead to a lower isolated yield. It is believed that more insoluble oligomers were generated in the presence of more FeCl₃. Reducing the reaction time led to a lower yield, while increasing the reaction time had no beneficial effect (Table 2, entries 5 and 6). When this reaction was performed without H₂O, only a trace amount of C₁₂₀O₂ was observed, indicating that H₂O was crucial for promoting this reaction (Table 2, entry 7). In addition, no benefit to this reaction could be achieved by varying the amount of H₂O (Table 2, entries 8 and 9). Decreasing the milling frequency to 35 Hz resulted in more C₁₂₀O and more recovered C₆₀, and increasing the milling frequency to 45 Hz did not improve the yield of C₁₂₀O₂ (Table 2, entries 10 and 11). In efforts to achieve more efficient synthesis of the peculiar $C_{120}O_2$, various Lewis acids, including AlCl₃, FeCl₂ and NiCl₂, and oxidizing agents, such as Oxone, m-chloroperbenzoic acid (m-CPBA) and H₂O₂, were explored. However, all of these additives were detrimental to the formation of $C_{120}O_2$ and afforded C_{120} exclusively (Table 2, entries 12-17). To compare the present solvent-free reaction with its liquid-phase counterpart, the reaction of C₆₀ (0.05 mmol) with FeCl₃ (0.50 mmol) and H₂O (0.75 mmol) was performed in 0.5 mL of 1,1,2,2-tetrachloroethane at 150 °C for 48 h. Neither the desired product C₁₂₀O₂ nor C120O could be isolated, and C120 was instead formed in 15% yield (Table 2, entry 18). Other solvents, including toluene, chlorobenzene or 1,2-C₆H₄Cl₂, were also examined. However, the generation of C₁₂₀O₂ could not be observed in any of these solvents. Thus, it is obvious that the present mechanochemical solvent-free protocol shows advantages and uniqueness compared to the corresponding liquid-phase reaction. On the basis of the results presented above, the optimized conditions to afford the bisfuranoid-bridged dimer C₁₂₀O₂ were determined as shown in entry 2 of Table 2: C₆₀ (0.05 mmol), FeCl₃ (0.50 mmol), H₂O (0.75 mmol), a milling frequency of 41.7 Hz and a milling time of 90 min. The HPLC chromatogram on a Cosmosil Buckyprep (4.6 × 250 mm) column with toluene as the eluent at a flow rate of 1 mL min⁻¹ and the detector wavelength at 326 nm is shown in Fig. 2. The retention times of C_{60} , $C_{120}O$ and $C_{120}O_2$ were 7.5 min, 18.1 min and 20.7 min, respectively. The isolated yield of C₁₂₀O₂ by HPLC on a Cosmosil Buckyprep-D (10 × 250 mm) column was 45%, which was dramatically higher than the overall yield of 0.1-1% for the three-step process starting from C_{60} (vide supra).

The molecular structures of $C_{120}O$ and $C_{120}O_2$ were unambiguously established by single-crystal X-ray crystallography and are shown in Fig. 3. The single-crystal structure of $C_{120}O$ reveals that it has a furanoid ring linking two fullerene cages via [6,6]-ring junctions, clarifying the uncertainty of the oxygen connectivity to fullerenes.¹² The single-crystal structure of $C_{120}O_2$ shows that the two fullerene cages are connected by adjacent furanoid rings via [6,6]-ring junctions as in the case of $C_{120}O$, resulting in a central four-membered-ring bridge via [5,6]-ring junctions. The obtained single-crystal structure of our $C_{120}O_2$ confirms that it has C_{2v} symmetry, is the most stable and

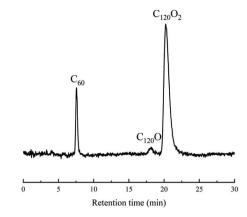


Fig. 2 HPLC chromatogram for the synthesis of $C_{120}O_2$ using FeCl₃ under optimal ball-milling conditions.

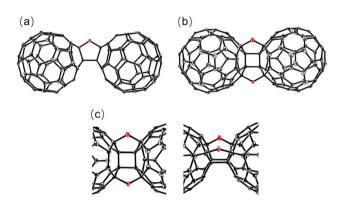


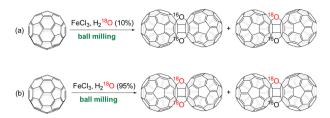
Fig. 3 ORTEP diagrams of (a) $C_{120}O$, (b) $C_{120}O_2$ and (c) top and side views around the two oxygen atoms in $C_{120}O_2$ with thermal ellipsoids shown at 10% probability. The solvent molecules were omitted for clarity.

plausible structure predicted by theoretical calculations⁸ and is neither the minor byproduct $C_{120}O_2$ with C_1 symmetry accompanying $C_{120}O$ from the solid–state reaction of C_{60} and $C_{60}O$ at 200 °C¹³ nor the $C_{120}O_2$ isomer with C_2 symmetry from the dimerization of [5,6]- $C_{60}O$.¹⁴ $C_{120}O$ and $C_{120}O_2$ were stable, and their thermogravimetric analyses (TGA) showed obvious weight loss above 370 °C (Fig. S5 and S6†).

To explore whether O_2 in the air atmosphere played a role during the milling process, the milling jar containing the reaction mixture was filled with nitrogen (N_2) in a glovebox and milled under the optimal conditions, which did not inhibit the production of $C_{120}O_2$ (Table 2, entry 19). When $C_{120}O$ was used to replace C_{60} under the optimal conditions, the yield of $C_{120}O_2$ decreased dramatically, and a considerable amount of C_{60} was produced (Table 2, entry 20). This result suggested that $C_{120}O_2$ was more likely to be generated directly from C_{60} rather than from $C_{120}O$ as a precursor. Therefore, $C_{120}O$ and $C_{120}O_2$ should be formed independently from C_{60} via different reaction pathways.

The mechanochemical $^{17}\text{O}/^{18}\text{O}$ labelling using $\text{H}_2^{17}\text{O}/\text{H}_2^{18}\text{O}$ has been reported. To further identify the source of the bridging oxygen atom in C_{120}O_2 , H_2^{18}O was introduced to the reaction system, and the reaction process was monitored by HRMS. When H_2^{18}O (10 atom % ^{18}O) was used, both $\text{C}_{120}^{16}\text{O}_2$

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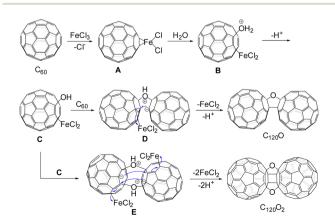


Scheme 2 $^{18}{\rm O}$ labelling experiments with (a) $\rm H_2^{18}O$ (10 atom % $^{18}O)$ and (b) $\rm H_2^{18}O$ (95 atom % $^{18}O)$.

and $C_{120}^{16}O^{18}O$ were observed (Scheme 2a and Fig. S7†). Next, the addition of $H_2^{18}O$ (95 atom % ^{18}O) under the optimal reaction conditions provided $C_{120}^{16}O^{18}O$ and $C_{120}^{18}O_2$ (Scheme 2b and Fig. S8†). These results reinforced the conclusion that the bridging oxygen atom in $C_{120}O_2$ originated from H_2O . Furthermore, when potassium ferricyanide was added to the reaction mixture, a dark blue precipitate was generated (Fig. S9†), indicating the presence of ferrous ions. More importantly, the X-ray photoelectron spectroscopy (XPS) measurement of the reaction mixture revealed that an Fe(n) species was generated after the reaction was completed (Fig. S10†).

On the basis of the above experimental results and the literature,16 a plausible reaction mechanism is outlined in Scheme 3. First, the initial coordination of C₆₀ with FeCl₃ provides the complex $FeCl_2(\eta^2-C_{60})$ (A), which is followed by the nucleophilic addition of H2O to afford intermediate B in a 1,4-addition pattern. Loss of H⁺ from intermediate B gives intermediate C. The hydroxy group in C directly attacks another molecule of pristine C₆₀ to form an oxonium-bridged zwitterionic dimer D. Then, intramolecular cyclization with the removal of FeCl₂ and H⁺ generates the furanoid-bridged dimer C₁₂₀O. With an increased amount of FeCl₃ and a higher milling frequency, the amount of the generated intermediate C can surpass that of the pristine C₆₀, and self-dimerization of C would dominate to give doubly oxonium-bridged intermediate E. Finally, E undergoes dual intramolecular cyclization with elimination of FeCl₂ and H⁺ to provide the bisfuranoid-bridged dimer $C_{120}O_2$.

Given that fullerene derivatives have been applied in organic solar cells (OSCs) as the third component, ¹⁷ preliminary results



Scheme 3 Proposed reaction mechanism.

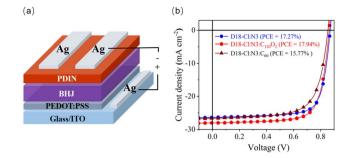


Fig. 4 (a) Schematic illustration of the OSC structure used in this work. (b) J-V curves of D18-Cl:N3 (blue line), D18-Cl:N3:C₁₂₀O₂ (red line) and D18-Cl:N3:C₆₀ (brown line)-based OSCs.

showed that C₁₂₀O₂ could be employed in OSCs with the of ITO/PEDOT:PSS/D18-Cl:N3:fullerene (1:1.4:0.12)/PDIN/Ag (Fig. 4). The device with $C_{120}O_2$ as the third component showed a PCE of 17.94% with a J_{SC} of 28.05 mA cm $^{-2}$, a $V_{\rm OC}$ of 0.86 V and an FF of 74.08%. The control device without a fullerene additive showed a lower PCE of 17.27% with a $J_{\rm SC}$ of 26.41 mA cm $^{-2}$, a $V_{\rm OC}$ of 0.87 V and an FF of 75.03%. The device with pristine C60 as the third component showed an inferior PCE of 15.77% with a $J_{\rm SC}$ of 26.68 mA cm⁻², a $V_{\rm OC}$ of 0.85 V and an FF of 69.24%. These results revealed that pristine C60 had an adverse effect, while the bisfuranoid-bridged dimer $C_{120}O_2$ was a promising third-component material in the active layer of the OSCs. Unfortunately, the synthesized C₁₂₀O has limited solubility and could not be used as a third component in the current OSCs.

Conclusions

In summary, we have disclosed the unexpected, divergent and highly efficient synthesis of furanoid-linked C120O and C120O2 from the FeCl₃-mediated mechanochemical reaction of C₆₀ with H₂O as the bridging oxygen source at room temperature under an air atmosphere. The present protocol avoids the usage of preprepared $C_{60}O$ and $C_{120}O$. The selective synthesis of $C_{120}O$ with one furanoid bridge and $C_{120}O_2$ with two furanoid bridges directly from pristine C60 can be achieved by altering the amount of FeCl₃ and the milling frequency. The excellent yields, simplicity of this synthetic process and solvent-free and ambient conditions compared to those of previous multistep processes make this mechanochemical protocol an efficient method for the divergent synthesis of $C_{120}O$ and $C_{120}O_2$. The specific structures of C₁₂₀O and C₁₂₀O₂ have been unequivocally established by single-crystal X-ray crystallography. A plausible reaction mechanism has been proposed based on the control experiments. The bisfuranoid-bridged dimer C₁₂₀O₂ has also been utilized as the third component in organic solar cells and has shown improved performance in OSC devices.

Data availability

The data supporting the findings of this study are available within the article and its ESI. \dagger

Author contributions

G.-W. W. and S. Y. supervised the project. G. S. and J.-S. C. performed experiments and data analysis and wrote original manuscript, Y.-Y. L. fabricated the organic solar cell devices and analyzed data. G. S., C. N., Z.-C. Y., Y.-R. Y. and M. C. characterized the X-ray structures. S.-Q. Y. performed XPS test and data analysis. X.-L. X. assisted in data analysis and original manuscript preparation. G.-W. W. acquired funding and wrote the manuscript. All the authors contributed with comments and revisions to the manuscript and gave approval to the final version.

Conflicts of interest

There are no conflicts to declare.

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