



Halogen bonded polypseudorotaxanes based on a pillar[5]arene host†

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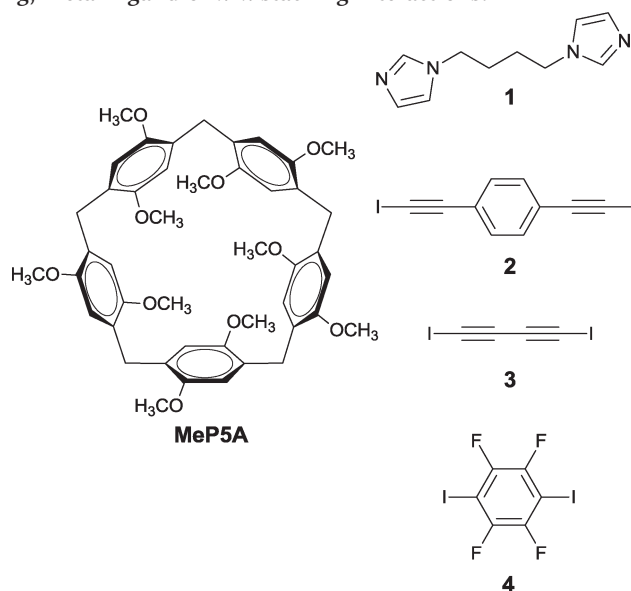
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Two crystalline supramolecular polypseudorotaxanes were obtained by combining permethylated pillar[5]arene as a macrocyclic wheel with 1,4-bis(1-imidazolyl)butane and 1,4-bis(iodoethynyl)benzene or 1,4-diiodo-1,3-butadiyne linked by C–I⋯N halogen bonds and creating a polyrotaxane axis. The resulting highly ordered supramolecular arrays were characterized by X-ray crystallography.

The synthesis of mechanically interlocked catenane and rotaxane assemblies has become a recent challenge in supramolecular chemistry not only for their unique structures but also due to their potential applications as molecular devices and functional materials.^{1,2} Among numerous interlocked structures constructed and studied in last few decades, polymers comprising rotaxane units have attracted considerable attention in the fields of materials science and nanotechnology.^{2,3} Polyrotaxanes and polypseudorotaxanes are constructed by threading macrocyclic rings, including cyclodextrins, crown ethers, cucurbiturils, calixarenes or pillararenes onto covalent type linear chains like polyethers, polyesters or polyamides, employing a variety of synthetic protocols. On the other hand, considerable efforts have been directed to the design of supramolecular polymers bearing rotaxane units self-assembled by highly directional and cooperative non-covalent interactions such as hydrogen bonding, host–guest interaction, π – π stacking or metal–ligand coordination.^{3–8} Due to the reversible, self-repairing and tunable nature of these interactions more advanced and useful

supramolecular structures can be obtained in a relatively simple way. However, the vast majority of these studies have been performed in solution, where the molecules are in a constant flux, and the degree of oligomerization and the structure of oligomers are strongly concentration dependent.^{3–6} Despite the fact that for future applications materials with high and controllable structural regularity are required, there are very few well-characterized examples of crystalline polyrotaxanes including 1D, 2D and 3D arrays assembled by hydrogen bonding, metal–ligand or π – π stacking interactions.⁸



In this paper, we report the synthesis and structural characterization of two crystalline supramolecular polypseudorotaxanes by combining permethylated pillar[5]arene (MeP5A) as a macrocyclic wheel with 1,4-bis(1-imidazolyl)butane (1) and 1,4-bis(iodoethynyl)benzene (2) or 1,4-diiodo-1,3-butadiyne (3) linked by halogen bonds and creating a polyrotaxane axis. Pillararenes, a new family of macrocyclic hosts, due to their symmetrical structure and rigid electron-rich cavity are ideal candidates as host molecules for the construction of rotaxanes or

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pseudorotaxanes and the research interest in this class of compounds has grown rapidly.⁹ The facile preparation and excellent binding abilities of peralkylated pillararenes towards neutral guest molecules in organic solvents make them superior to water soluble cyclodextrins or cucurbiturils, possessing nearly the same cavity sizes as the host molecules for the fabrication of new supramolecular architectures. Thus we selected MeP5A as a host and bisimidazolyl derivative **1** as a guest due to their reported high association constant in nonpolar solvents [K_a of $(4.7 \pm 0.3) \times 10^3 \text{ M}^{-1}$].¹⁰ The encapsulated by multiple C–H $\cdots\pi$ and C–H \cdots O interactions molecule of **1** possessing two unscreened imidazole nitrogen atoms should be able to further interact with halogen bond donors **2** or **3** and create a polymeric rotaxane axis. Halogen bonding has promising potential in supramolecular chemistry, particularly, as a design element in crystal engineering and molecular recognition.¹¹ Heavier halogens, due to an anisotropic distribution of electrostatic potential, exhibit electrophilic characteristics and can interact with electron-pair donating heteroatoms (O, N, S) or anions. Since iodine atoms connected to C(sp) atoms form the strongest halogen bonds¹² the iodoalkynes **2** and **3** were chosen as components of the polypseudorotaxane axis. Furthermore, due to a lesser steric overcrowding they are better accessible to the imidazole nitrogen atoms of **1** than the iodine atoms in fluorinated iodobenzenes, most frequently used as halogen bond donors.¹³ Obtaining three component cocrystals with predictable connectivity is obviously an extremely difficult task.¹⁴ Indeed, our initial attempt to crystallize an equimolar mixture of MeP5A, **1** and **2** afforded only a binary complex **1-2** composed of infinite chains of the halogen bonded components. However, preparation of pseudorotaxane MeP5A-**1** from equimolar amounts of MeP5A and **1** in toluene–chloroform followed by its cocrystallization with **2** from the 1:2 mixture of tetrachloromethane and dichloromethane gave solvated crystals of the polypseudorotaxane MeP5A-**1-2**-(CCl₄)₂. The second ternary complex MeP5A-**1-3**-(toluene)_{1.5} was obtained in an analogous way (Fig. 2).[‡]

Triclinic crystals of MeP5A-**1-2**[§] and MeP5A-**1-3**[¶] contain infinite chains of alternating **1** and **2** or **1** and **3** molecules, respectively, connected by halogen bonds forming the polypseudorotaxane axis with the threaded pillararene MeP5A beads (Fig. 1). The halogen bonds connecting **1** with **2** or **1** with **3** are nearly linear (the C–I \cdots N angles are 172°) and quite strong as evidenced by the I \cdots N distances of 2.734–2.794 Å (77–79% of the sum of the van der Waals radii of I and N).¹⁵ The diimidazolylbutane unit **1** is accommodated

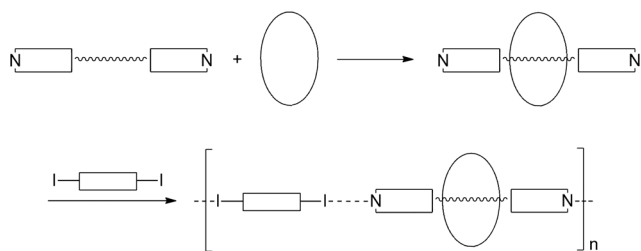


Fig. 1 Halogen bonded polypseudorotaxane formation in the solid state.

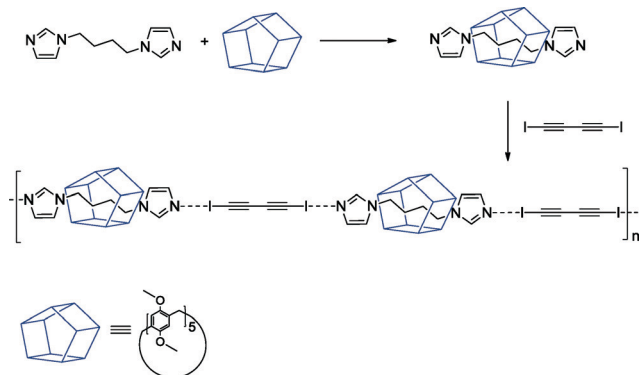


Fig. 2 Schematic representation of the approach for the formation of designed polypseudorotaxanes.

centrally within the macrocycle with the MeP5A mean plane passing through the middle of the aliphatic (CH₂)₄ chain. Nevertheless the conformation of **1** differs in the two crystal structures: in MeP5A-**1-2** the aliphatic chain of **1** adopts a folded conformation, whereas in MeP5A-**1-3** it is fully extended.||

It is noteworthy that pillararene molecules assume a planar chiral conformation and their racemization occurs by rotation of the hydroquinone units.^{9a,16} Obviously, the synthesized pillar[5]arenes are racemic mixtures. Thus a close inspection of the structure of MeP5A-**1-2** reveals that the polyrotaxane thread is composed of alternating *pR* and *pS* enantiomers of the MeP5A units. Furthermore, the pillararene chirality induces chiral conformations of the included guest molecules of **1** (Fig. 3). In contrast, the MeP5A-**1-2** threads are built from the homochiral MeP5A molecules and the neighboring threads contain the molecules of the opposite chirality.

It should be emphasized that the above polypseudorotaxane structures exist only in the solid state and their dissolution simply results in their dissociation and disassembly. This is due to the relatively low association constants of iodoethynyl derivatives and halogen bond acceptors in solution.¹⁷ The only interaction between the components

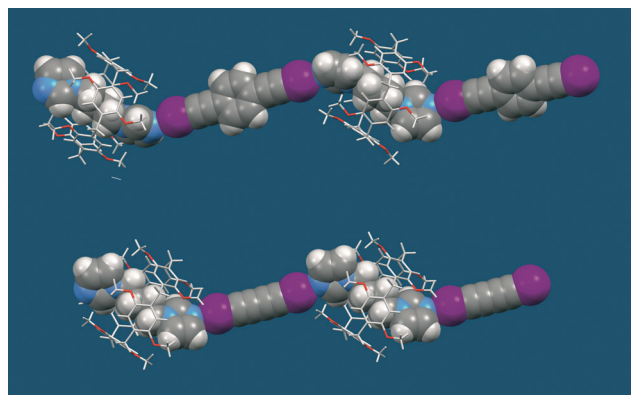


Fig. 3 Molecular structures of polypseudorotaxanes MeP5A-**1-2** (top) and MeP5A-**1-3** (bottom) formed via halogen bonds.



that occurs in solution is a complexation equilibrium between pillararene MeP5A and bisimidazole 1 that is reflected by the corresponding ^1H and ^{13}C NMR spectra (see the ESI †).^{9a}

In summary, we have presented the first two pseudorotaxanes containing pillararene beads self-assembled with use of halogen bonds. A key to the success of the self-assembly of three-component supermolecules was the high affinity of pillararene MeP5A towards diimidazolylbutane derivative 1 which allowed the formation of a relatively stable pseudorotaxane. In addition, the highly symmetrical structure of the pillararene and its solubility in organic solvents facilitated the manipulation and crystallization of the complexes with structural regularity. Our work has demonstrated that with use of crystal engineering methods highly ordered and predictable complex supramolecular arrays may be readily accessible in a relatively simple way.

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Notes and references

† X-Ray diffraction data were collected with an Oxford Diffraction Supernova diffractometer and processed with the CrysAlis software.¹⁸ The crystal structures were solved with SIR2004 (ref. 19) and refined by full-matrix least-squares with SHELXL-2014 (ref. 20) within Olex-2.²¹ Drawings were prepared with Mercury²² software.

§ Crystal data for MeP5A-1-2: $\text{C}_{45}\text{H}_{50}\text{O}_{10}\cdot\text{C}_{10}\text{H}_{14}\text{N}_4\cdot\text{C}_{10}\text{H}_4\text{I}_2\cdot 2(\text{CCl}_4)$ ($M = 1626.65$ g mol $^{-1}$), crystal size $0.3 \times 0.2 \times 0.02$ mm 3 , triclinic, space group $P\bar{1}$ (no. 2), $a = 12.6235(2)$ Å, $b = 16.2250(4)$ Å, $c = 18.6220(4)$ Å, $\alpha = 90.7497(18)^\circ$, $\beta = 103.7900(18)^\circ$, $\gamma = 102.4114(17)^\circ$, $V = 3609.24(13)$ Å 3 , $Z = 2$, $D_c = 1.497$ g cm $^{-3}$, $\mu(\text{CuK}\alpha) = 10.036$ mm $^{-1}$, $T = 130$ K, Cu K α radiation ($\lambda = 1.54184$ Å), 58 888 reflections measured ($9.84^\circ \leq 2\theta \leq 149.008^\circ$), 14 769 unique ($R_{\text{int}} = 0.0590$, $R_{\text{sigma}} = 0.0489$) which were used in all calculations. The final R_1 was 0.0544 ($I > 2\sigma(I)$) and wR_2 was 0.1513 (all data). One of the methoxy methyl groups and one of the imidazolyl groups were refined as disordered over two positions.

¶ Crystal data for MeP5A-1-3: $\text{C}_{45}\text{H}_{50}\text{O}_{10}\cdot\text{C}_{10}\text{H}_{14}\text{N}_4\cdot\text{C}_4\text{I}_2\cdot 1.5(\text{C}_7\text{H}_8)$ ($M = 2762.28$ g mol $^{-1}$), crystal size $0.4 \times 0.35 \times 0.2$ mm 3 , triclinic, space group $P\bar{1}$ (no. 2), $a = 11.6992(1)$ Å, $b = 14.9802(2)$ Å, $c = 20.2256(3)$ Å, $\alpha = 72.161(1)^\circ$, $\beta = 83.489(1)^\circ$, $\gamma = 73.806(1)^\circ$, $V = 3238.85(7)$ Å 3 , $Z = 2$, $D_c = 1.416$ g cm $^{-3}$, $\mu(\text{CuK}\alpha) = 8.116$ mm $^{-1}$, $T = 130$ K, Cu K α radiation ($\lambda = 1.54184$ Å), 80 767 reflections measured ($4.59^\circ \leq 2\theta \leq 153.03^\circ$), 13 528 unique ($R_{\text{int}} = 0.0537$, $R_{\text{sigma}} = 0.0239$) which were used in all calculations. The final R_1 was 0.0359 ($I > 2\sigma(I)$) and wR_2 was 0.0991 (all data). Both toluene molecules are disordered and one of them is disordered around an inversion center.

|| Crystal data for MeP5A-1-4: $\text{C}_{45}\text{H}_{50}\text{O}_{10}\cdot\text{C}_{10}\text{H}_{14}\text{N}_4\cdot 2(\text{C}_6\text{F}_4\text{I}_2)\cdot 2(\text{H}_2\text{O})$ ($M = 1780.85$ g mol $^{-1}$), orthorhombic, space group $Pbcn$ (no. 60), $a = 20.04603(13)$ Å, $b = 23.88917(14)$ Å, $c = 14.22073(10)$ Å, $V = 6810.07(8)$ Å 3 , $Z = 4$, $D_c = 1.737$ g cm $^{-3}$, $\mu(\text{CuK}\alpha) = 15.107$ mm $^{-1}$, $T = 130$ K, Cu K α radiation ($\lambda = 1.54184$ Å), 66 932 reflections measured ($13.10^\circ \leq 2\theta \leq 149.00^\circ$), 6952 unique ($R_{\text{int}} = 0.0498$, $R_{\text{sigma}} = 0.0213$) which were used in all calculations. The final R_1 was 0.0460 ($I > 2\sigma(I)$) and wR_2 was 0.1041 (all data). The molecule of 1 and one of the water molecules have half occupancy and are disordered over a twofold symmetry axis.

- (a) D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, 95, 2725; (b) M. Xue, Y. Yang, X. Chi, X. Yan and F. Huang, *Chem. Rev.*, 2015, 115, 7398.

- (a) T. Takata, *Polym. J.*, 2006, 38, 1; (b) F. M. Raymo and J. F. Stoddart, *Chem. Rev.*, 1999, 99, 1643.
- (a) A. Harada, A. Hashidzume, H. Yamaguchi and Y. Takashima, *Chem. Rev.*, 2009, 109, 5974; (b) A. Harada, Y. Takashima and H. Yamaguchi, *Chem. Soc. Rev.*, 2009, 38, 875; (c) C. Li, *Chem. Commun.*, 2014, 50, 12420; (d) L. Yang, X. Tan, Z. Wang and X. Zhang, *Chem. Rev.*, 2015, 115, 7196.
- (a) M. Miyauchi and A. Harada, *J. Am. Chem. Soc.*, 2004, 126, 11418; (b) M. Miyauchi, T. Hoshino, H. Yamaguchi, S. Kamitori and A. Harada, *J. Am. Chem. Soc.*, 2005, 127, 2034; (c) Y. Hasegawa, M. Miyauchi, Y. Takashima, H. Yamaguchi and A. Harada, *Macromolecules*, 2005, 38, 3724; (d) K. Ohga, Y. Takashima, H. Takahashi, Y. Kawaguchi, H. Yamaguchi and A. Harada, *Macromolecules*, 2005, 38, 5897; (e) P. Kuad, A. Miyawaki, Y. Takashima, H. Yamaguchi and A. Harada, *J. Am. Chem. Soc.*, 2007, 129, 12630; (f) A. Miyawaki, M. Miyauchi, Y. Takashima, H. Yamaguchi and A. Harada, *Chem. Commun.*, 2008, 456.
- (a) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, 50, 1397; (b) N. L. Strutt, H. Zhang, M. A. Giesener, J. Leia and J. F. Stoddart, *Chem. Commun.*, 2012, 48, 1647; (c) T. Ogoshi, H. Kayama, D. Yamafuji, T. Aoki and T. Yamagishi, *Chem. Sci.*, 2012, 3, 3221; (d) Y. Guan, M. Ni, X. Hu, T. Xiao, S. Xiong, C. Lin and L. Wang, *Chem. Commun.*, 2012, 48, 8529; (e) B. Xia, B. Zheng, C. Han, S. Dong, M. Zhang, B. Hu, Y. Yub and F. Huang, *Polym. Chem.*, 2013, 4, 2019; (f) C. Han, B. Xia, J. Chen, G. Yu, Z. Zhang, S. Dong, B. Hu, Y. Yub and M. Xue, *RSC Adv.*, 2013, 3, 16089; (g) C. Li, K. Han, J. Li, Y. Zhang, W. Chen, Y. Yu and X. Jia, *Chem. – Eur. J.*, 2013, 19, 11892; (h) S. Wang, Y. Wang, Z. Chen, Y. Lin, L. Weng, K. Han, J. Li, X. Jia and C. Li, *Chem. Commun.*, 2015, 51, 3434; (i) B. Shi, K. Jie, Y. Zhou, D. Xia and Y. Yao, *Chem. Commun.*, 2015, 51, 4503.
- (a) X.-Y. Hu, X. Wu, Q. Duan, T. Xiao, C. Lin and L. Wang, *Org. Lett.*, 2012, 4826; (b) X.-Y. Hu, P. Zhang, X. Wu, W. Xia, T. Xiao, J. Jiang, C. Lin and L. Wang, *Polym. Chem.*, 2012, 3, 3060; (c) X.-Y. Hu, X. Wu, S. Wang, D. Chen, W. Xia, C. Lin, Y. Pan and L. Wang, *Polym. Chem.*, 2013, 4, 4292.
- (a) Y. Liu, Y.-L. Zhao, H.-Y. Zhang and H.-B. Song, *Angew. Chem., Int. Ed.*, 2003, 42, 3260; (b) Y. Liu, S.-H. Song, Y. Chen, Y.-L. Zhao and Y.-W. Yang, *Chem. Commun.*, 2005, 1702.
- (a) M. Asakawa, P. R. Ashton, G. R. Brown, W. Hayes, S. Menzer, J. F. Stoddart, A. J. P. White and D. J. Williams, *Adv. Mater.*, 1996, 8, 37; (b) D. Whang, Y.-M. Jeon, J. Heo and K. Kim, *J. Am. Chem. Soc.*, 1996, 118, 11333; (c) D. Whang and K. Kim, *J. Am. Chem. Soc.*, 1997, 119, 451; (d) E. Lee, J. Heo and K. Kim, *Angew. Chem., Int. Ed.*, 2000, 39, 2699; (e) C. S. A. Fraser, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2001, 1310; (f) G. J. E. Davidson and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2003, 42, 74; (g) D. J. Hoffart and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2005, 44, 901; (h) H.-Y. Gong, B. M. Rambo, W. Cho, V. M. Lynch, M. Oh and J. L. Sessler, *Chem. Commun.*, 2011, 47, 5973; (i) X.-S. Wu, J. Liang, X.-L.



- Hu, X.-L. Wang, B.-Q. Song, Y.-Q. Jiao and Z.-M. Su, *Cryst. Growth Des.*, 2015, **15**, 4311.
- 9 (a) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **47**, 1294; (b) T. Ogoshi and T. Yamagishi, *Eur. J. Org. Chem.*, 2013, 2961; (c) N. L. Strutt, H. Zhang, S. T. Schneebeli and J. F. Stoddart, *Acc. Chem. Res.*, 2014, **47**, 2631; (d) L.-L. Tan and Y.-W. Yang, *J. Inclusion Phenom. Macrocyclic Chem.*, 2015, **81**, 13.
- 10 (a) C. Li, S. Chen, J. Li, K. Han, M. Xu, B. Hu, Y. Yuc and X. Jia, *Chem. Commun.*, 2011, **47**, 11294; (b) K. Han, Y. Zhang, J. Li, Y. Yu, X. Jia and C. Li, *Eur. J. Org. Chem.*, 2013, 2057; (c) The perethylated pillar[5]arene (EtP5A) has a four times higher value of association constant compared with **1** but in the case of MeP5A the nitrogen atoms of the guest molecule are better accessible to halogen bond donors.
- 11 (a) P. Metrangolo and G. Resnati, *Halogen Bonding: Fundamentals and Applications (Structure and Bonding)*, Springer, Heidelberg, 2010; (b) A. Priimagi, G. Cavallo, P. Metrangolo and G. Resnati, *Acc. Chem. Res.*, 2013, **46**, 2686; (c) L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney and P. D. Beer, *Chem. Rev.*, 2015, **115**, 7118; (d) G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.*, 2016, **116**, 2478.
- 12 E. Bosh, *Cryst. Growth Des.*, 2014, **14**, 126.
- 13 Our attempts to use 1,4-diiodotetrafluorobenzene (**4**) as the axis component afforded the crystals of MeP5A-1-**4**₂·2 (H₂O), where the pseudorotaxane MeP5A-1 is halogen bonded to only one molecule of **4** (the C–I···N halogen bond is relatively weak; I···N 3.311 Å) and the water molecules are hydrogen bonded to the imidazole nitrogen of **1** and halogen bonded to the iodine atoms of **4** (I···O 2.885–2.978 Å). For more details see the ESI†.
- 14 (a) C. B. Aakeröy, A. M. Beatty and B. A. Helfrich, *Angew. Chem., Int. Ed.*, 2001, **40**, 3240; (b) C. B. Aakeröy, J. Desper and J. F. Urbina, *Chem. Commun.*, 2005, 2820.
- 15 A. Bondi, *J. Phys. Chem.*, 1966, **70**, 3006.
- 16 (a) T. Ogoshi, K. Masaki, R. Shiga, K. Kitajima and T. Yamagishi, *Org. Lett.*, 2011, **13**, 1264; (b) N. L. Strutt, D. Fairen-Jimenez, J. Iehl, M. B. Lalonde, R. Q. Snurr, O. K. Farha, J. T. Hupp and J. F. Stoddart, *J. Am. Chem. Soc.*, 2012, **134**, 17436.
- 17 O. Dumele, D. Wu, N. Trapp, N. Goroff and F. Diederich, *Org. Lett.*, 2014, **16**, 4722.
- 18 *CrysAlis PRO Software*, Agilent Technologies, Yarnton, Oxfordshire, England, 2014.
- 19 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascaran, L. De Caro, C. Giacovazzo, G. Polidori and R. J. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381.
- 20 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.
- 21 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
- 22 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466.

