Electronic Supplementary Material (ESI) for CrystEngComm.

Crystal and Molecular Structure of Series of Triphilic Ionic Liquid-Crystalline Materials based on the 1,2,4-Triazolium Cation

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SUPPLEMENTARY INFORMATION

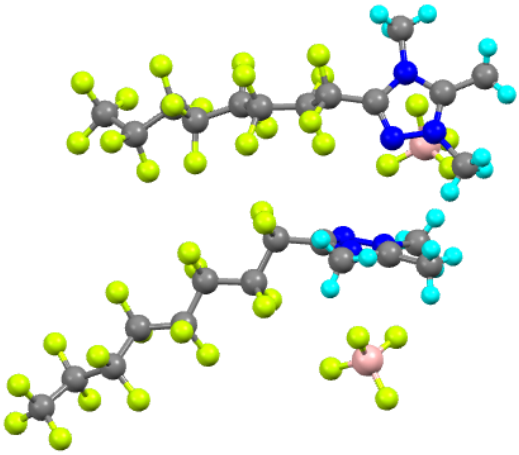
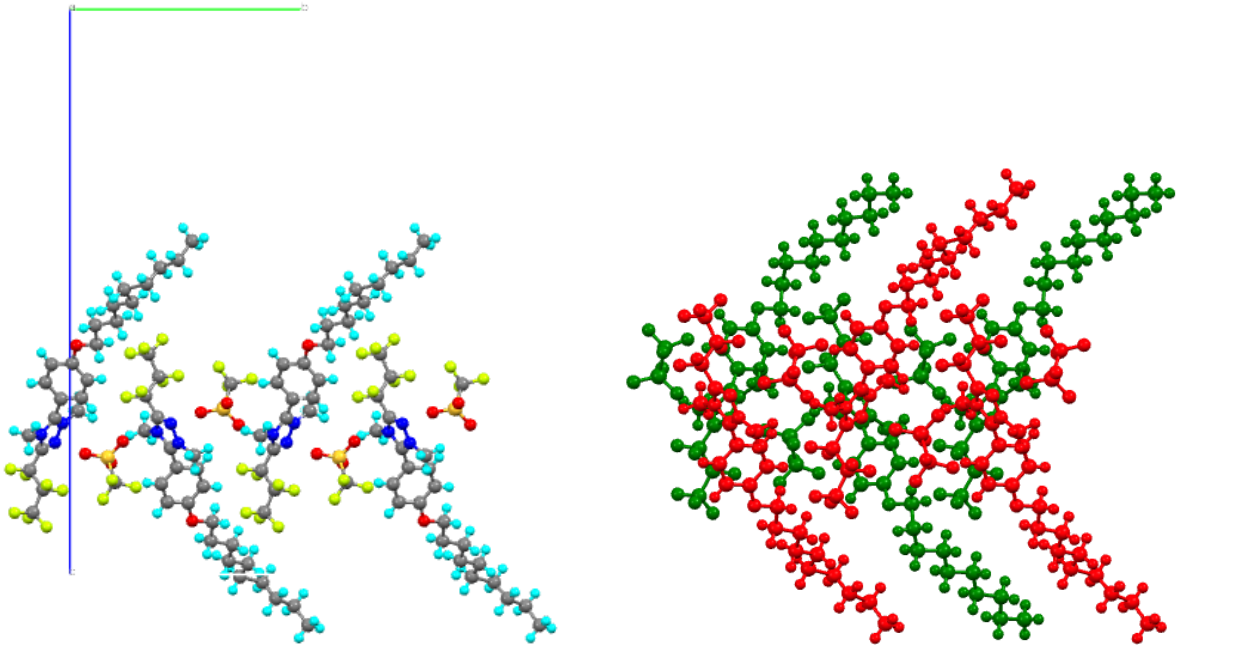


Figure S1 Structure of 1,2,4-trimethyl-3-perfluorooctyl-1,2,4-triazolium tetrafluoroborate showing cation···anion interaction.



(a) (b)

Figure S2 (a) Propagation of Cation 2 of [TRYUM-3,10][OTf] viewed down the crystallographic *a*-axis; (b) Propagation of both Cation 1 (green) and Cation 2 (red) of [TRYUM-3,10][OTf] viewed down the crystallographic *a*-axis (position of axes identical to Fig. S2a).

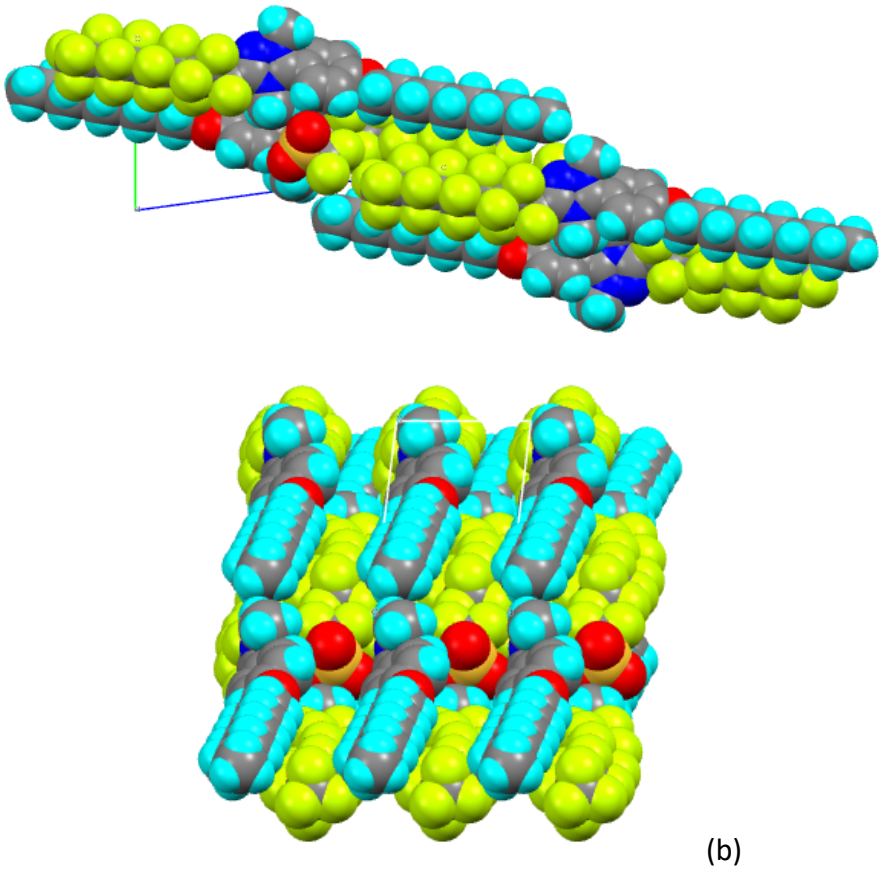


Figure S3 Views of the structure and packing of [TRYUM-9,10][OTf] viewed down (a) the *a*-axis, (b) the *c*-axis.

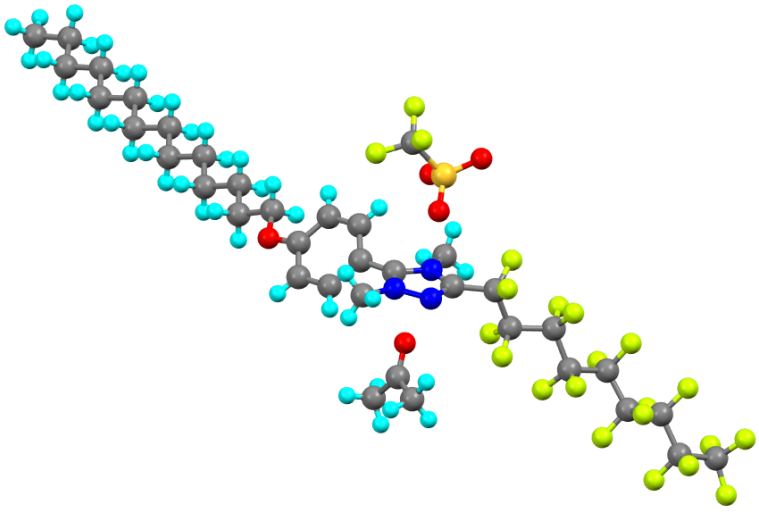


Figure S4 Molecular structure of [TRYUM-9,14][OTf] showing the interaction of the cation ring with the triflate anion and the acetone solvate.

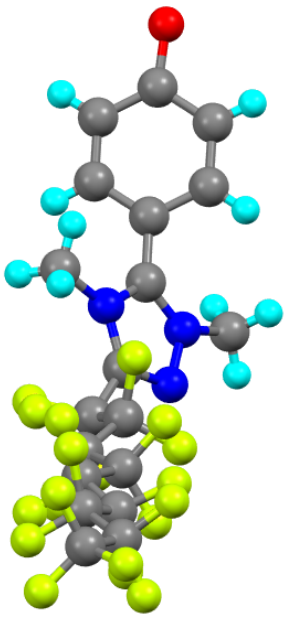


Figure S5 Truncated structure of [TRYUM-9,14][OTf] showing an end-on view of the perfluorocarbon chain and the non-helical propagation.

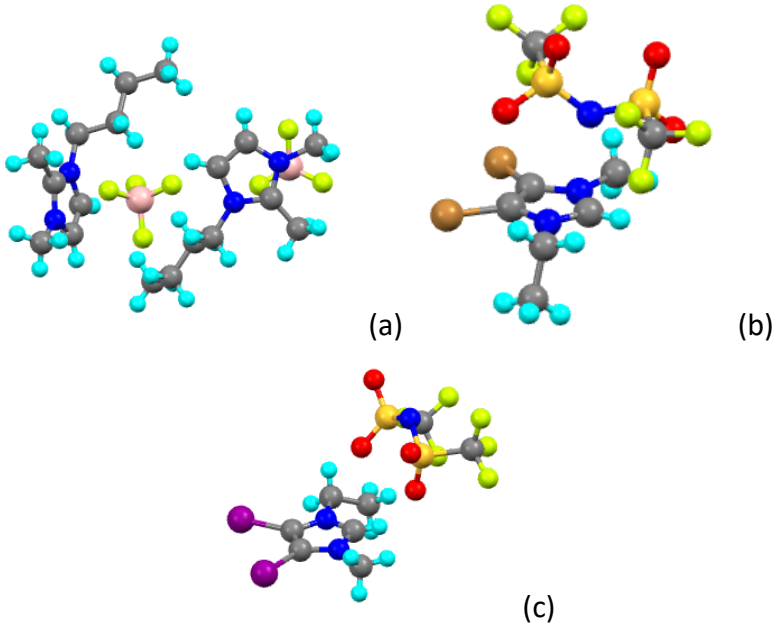


Figure S6 Example structures from the Cambridge database showing facial anion…cation interactions: (a) 1,2-dimethyl-3-butylimidazolium tetrafluoroborate (EZILII01)[1], (b) 1-ethyl-3-methyl-4,5-dibromoimidazolium bistriflimide (AGOCIK)[2] and (c) 1-ethyl-3-methyl-4,5-diiodoimidazolium bistriflimide (AGOCOQ).[2]

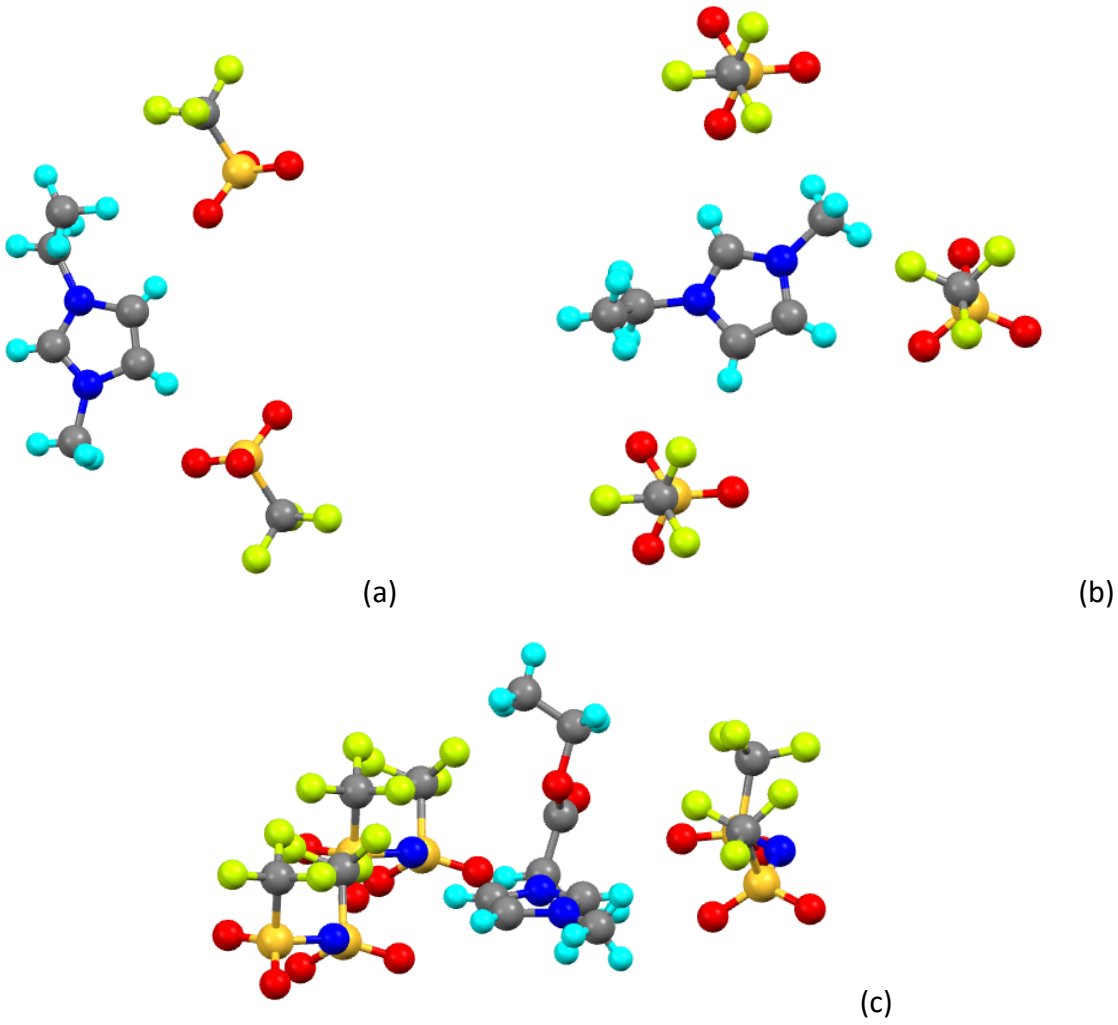


Figure S7 Example structures from the Cambridge database showing anion…hydrogen interactions: (a) 1-ethyl-3-methylimidazolium triflate•18-crown-6 (crown ether not shown for clarity - QITXOH);[3] (b) 1-ethyl-3-methylimidazolium triflate (RENSIN) and[4] (c) 1-(1-(Ethoxycarbonyl)ethyl)-3-methylimidazolium bis(triflimide) (IZUZAE).[5]

Structure of [TRYUM-3,14][Tf_2N]

The structure, which is in $P2_1$, is similar to the other triflimides reported in the main manuscript in having facial cation···anion···cation propagation and a segregated structure of chains. Representative images are shown as Fig. S8.

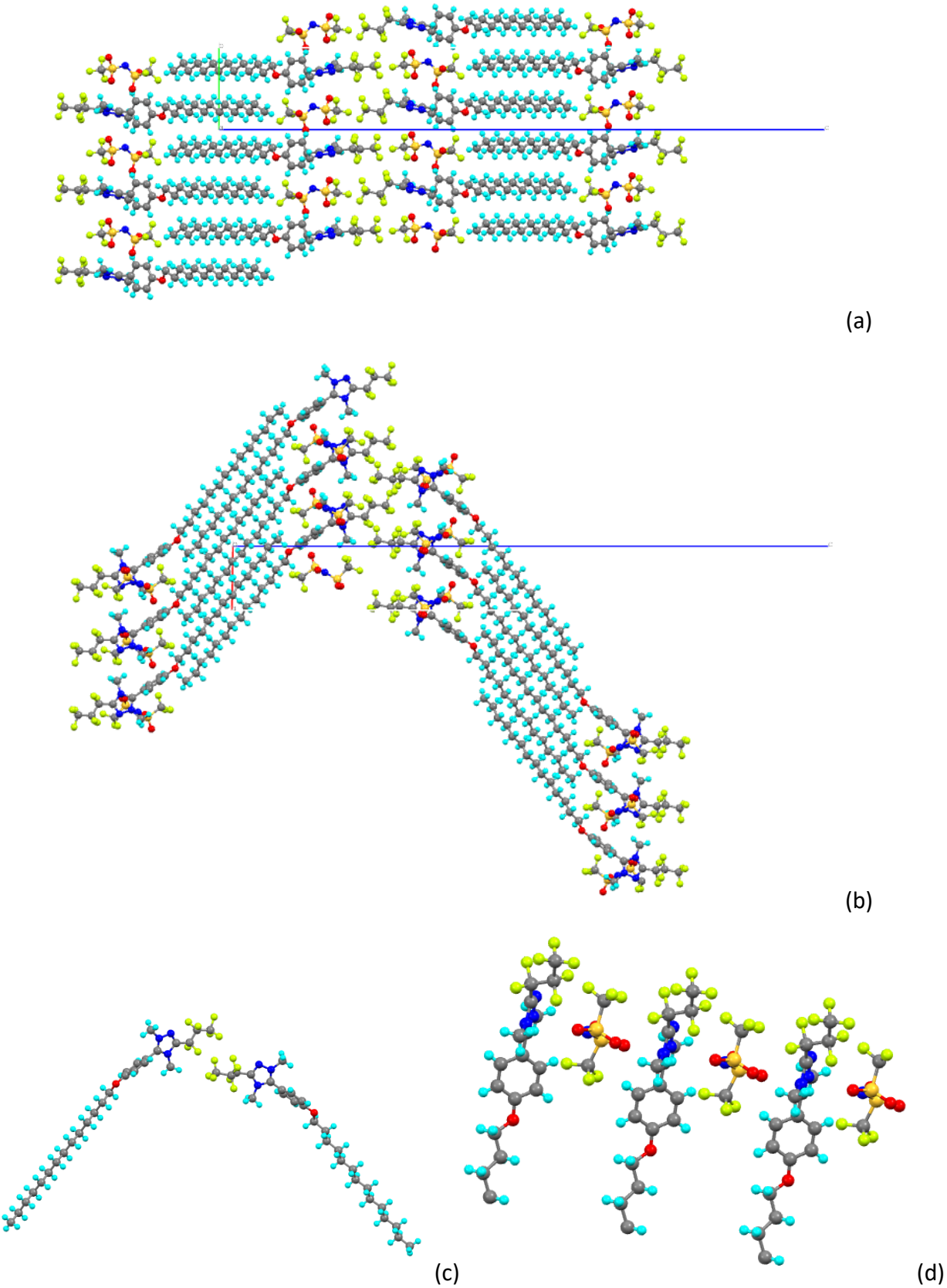


Figure S8 [TRYUM-3,14][Tf_2N] viewed: (a) down the *a*-axis, (b) down the *b*-axis, (c) relative disposition of two cations and (d) showing propagation of the cations and anions through facial interactions with the cation.

Description of the Computational Work

DFT studies were performed on the model trazolium cation shown in Fig. 12 in the main section. Geometry optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. Minima were confirmed as such by the absence of imaginary frequencies. No symmetry constraints were applied during optimisations. These steps were performed using the TURBOMOLE 6.4 package using the resolution of identity (RI) approximation.[6] Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the flexible def2-TZVPP basis set using GAUSSIAN 09 revision D.01 in order to prepare input files for use by the NBO software.[7] NBO analysis was performed using NBO 7.0.5 and gas-phase partial charges reported in Fig. 12 in the main section are derived from the natural population analysis.[8] Structures were visualised and modified using Facio,[9] Jmol,[10] and gOpenMol.

XYZ coordinates

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C	-0.09604	0.76997	-2.93357
C	-0.98784	-0.13991	-2.29957
H	-1.73809	-0.65218	-2.92096
C	-0.91943	-0.35974	-0.92935
H	-1.64366	-1.04522	-0.46105
C	0.03797	0.33127	-0.13140
C	0.92464	1.23860	-0.76796
H	1.70061	1.75924	-0.18406
C	0.86937	1.45360	-2.14677
H	1.58635	2.14678	-2.60857
C	0.10706	0.11309	1.30522
C	0.22410	0.39035	3.49285
C	0.10177	2.52632	2.10009
H	-0.51368	2.95866	2.91134
H	-0.37414	2.72926	1.12139
H	1.11712	2.97012	2.12931
C	0.11046	-2.43100	1.41671
H	0.78192	-3.05130	2.04173
H	0.47738	-2.39526	0.37291

H	-0.91614	-2.85184	1.44858
C	0.28704	1.09143	4.83454
C	0.58938	0.16111	6.05736
F	0.63355	0.91319	7.15957
C	0.60126	1.82247	-4.99845
H	1.66228	1.50314	-4.87813
H	0.48842	2.84545	-4.57095
C	0.16947	1.77852	-6.45296
H	-0.88876	2.09654	-6.56372
H	0.27829	0.75510	-6.87016
H	0.80503	2.46746	-7.04905
F	-0.90184	1.72283	5.05295
F	1.26287	2.04225	4.77250
F	-0.37121	-0.76191	6.18547
F	1.77492	-0.44056	5.87637
N	0.11708	-1.07559	1.96862
N	0.17897	-0.90980	3.31272
N	0.17245	1.06973	2.28773
O	-0.24495	0.91182	-4.25333

References

S1 C. Pulham, J. Pringle, A. Parkin, S. Parsons and D. Messenger, *CSD Communication*, 2005, DOI:10.5517/cc992pb.

S2 T. Mukai and K. Nishikawa, *RSC Adv.*, 2013, **3**, 19952-19955.

S3 M. Gjikaj, W. Brockner, J. Namyslo and A. Adam, *CrystEngComm*, 2008, **10**, 103-110.

S4 A.R. Choudhury, N. Winterton, A. Steiner, A.I. Cooper and K.A. Johnson, *CrystEngComm*, 2006, **8**, 742-745.

S5 J.J. Jodry and K. Mikami, *Tetrahedron Lett.*, 2004, **45**, 4429-4431.

S6 a) P. Csaszar, P. Pulay, *J. Mol. Struct.* 1984, **114**, 31-34; b) R. Ahlrichs, M. Bar, M. Haser, H. Horn, C. Kolmel, *Chem. Phys. Lett.*, 1989, **162**, 165-169; c) K. Eichkorn, O. Treutler, H. Ohm, M. Haser, R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283-289; d) O. Treutler, R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346-354; e) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.,* 1997, **97**, 119-124; f) M. von Arnim, R. Ahlrichs, *J. Chem. Phys.*, 1999, **111**, 9183-9190; g) P. Deglmann, F. Furche, *J. Chem. Phys.*, 2002, **117**, 9535-9538; h) P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.*, 2002, **362**, 511-518; i) P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.*, 2004, **384**, 103-107; j) A. Baldes, F. Weigend,

Mol. Phys., 2013, **111**, 2617-2624; k) F. Furche, R. Ahlrichs, C. Hattig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.*, 2014, **4**, 91-100.

S7 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

S8 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2018.

S9 M. Suenaga, *J. Comput. Chem Jpn.* 2005, **4**, 25-32.

S10 http://jmol.sourceforge.net/