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Host-guest inclusion complexes formed between a symmetrical tetrasubstituted cucurbit[6]uril and glycine

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Herein, we have investigated the host-guest inclusion complexes formed on interaction of the symmetric tetramethyl-substituted cucurbit[6]uril (TMeQ[6]) with glycine (Gly) under different conditions. The interactions have been studied both in solution (by ^{1}H NMR spectroscopy and mass spectrometry) and in the solid state by single crystal X-ray diffraction. The molecular structures of two products are reported, namely TMe[Q6].$(H_2O)_2(PO_4)(NH_3CH_2COOH)_2$ (**1**) and TMe[Q6].$Ca(H_2O)_5.(Cl)_3(NH_3CH_2COOH).16H_2O$ (**2**). Complex **1** adopts a hydrogen-bonded dimeric structure with two glycinium ions contained within a TMeQ6 molecule with the NH_3^+ portions of the two molecules located just above the opposite rims of the bowl and forming hydrogen bonds with C-O. In **2**, there are centrosymmetric dimers bridged by pairs of calcium ions.

Introduction

There is considerable interest in systems that allow for the dimerization of amino acids, and such studies are driven in part by investigations into the origin of life.[1] With this in mind, a number of studies have focused on the simplest of the amino acids, namely glycine, as a way to obtain useful information into the origins of polypeptide formation, and to further understand its potential application in biological activity. For example, Shields *et al*. have recently reported DFT and configurational sampling studies[2] that show glycine dimerization can be promoted by the presence of water molecules. Moreover, the same group has also investigated the catalytic properties of water molecules for gas phase glycine dimerization at different temperatures, and found that at temperatures associated with the lower parts of the earth's atmosphere, the catalytic influence in enhanced *versus* higher temperatures.[3] An understanding of the role played by amino acids in living systems can be applied in fields such as nutritional analysis, medical diagnostics, and cell imaging. Indeed, scientists have been attracted to the idea of artificial containers that can recognize and include amino acids.[4-8] To date, a variety of macrocyclic hosts including cyclodextrins, cyclophanes, calix[*n*]arenes and pillar[*n*]arenes have been investigated for their ability to recognize and encapsulate amino acids.[9-11] Our research in this area focuses on the use of cucurbit[*n*]urils (n = 5-8, 10, 13-15, abbreviated as Q[*n*]), a class of macrocyclic molecule consisting of n glycoluril units bridged by 2n methylene groups. Q[*n*]s are emerging as a versatile family of macrocycles, and the presence of the cavity is facilitating studies into their inclusion chemistry.[12] In turn, this is leading to new methods of detection, sensing and delivery of the encapsulated guests.[13] In this area, the detection of amino acids (and peptides and proteins) has attracted attention,[14] and a number of early studies reported thermodynamic data using techniques such as calorimetric titrations and spectroscopic methods.[15,16] Results revealed the potential for the sensing of specific peptides, as well as an ability to discriminate amino acids from amine.[17] Several supramolecular systems that can recognize specific amino acids or their residues in peptides and proteins have been developed. The structures of a number of glycyl-containing dipeptide Q[6] complexes were investigated by Danylyk, and a number of interactions (involving ion-dipole or hydrogen bonding) were observed in the resulting exclusion complexes.[18] Moreover, Crowley *et al* reported the use of Q[6] for protein recognition, where *N*-terminal recognition was noted.[19] We[20] and others[21] have more recently successfully used a number of cucurbit[*n*]uril-based systems to encapsulate the likes of L-valine, D-leucine, D-methionine and phenylalanine.[20a, b] Results in the gas phase and solution highlighted the importance of entropic and desolvation penalties that impacted greatly on the binding affinity.[20a] Moreover, inverted Q[7] as another host molecule, was also used to study the binding interactions with 10 essential amino acids,Arg, Met, Lys, Ile, His,Leu,Trp, Val,Thr and Phe.[20d] In this contribution, we turn our attention to the use of the alkyl-

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substituted cucurbit[6]uril TMeQ[6], which is known to exhibit enhanced solubility (*versus* the parent Q[6]) in aqueous solution.[22] In particular, we investigate the ability of TMeQ[6] to recognize glycine (Gly). Solution studies indicate *endo* binding between Gly and TMeQ[6], which remains unaffected by the addition of small amounts of Ca^{2+} (which resides exo to the cavity). In the solid state, the structures of two interesting dimeric products have been determined using single crystal X-ray diffraction. The use of calcium salts to promote structure elucidation of Q[*n*] systems dates back to the early 1980s.[23]

Results and Discussion

The binding interactions of TMeQ[6] toward the guest Gly were first investigated in aqueous solution using ^{1}H NMR spectroscopy. As shown in Figure 1, the methylene proton Hα of Gly in D_2O exhibits only a resonance signal. On gradual addition of TMeQ[6] into the aqueous solution of Gly, two sets of signals for the methylene proton Hα of Gly were observed; one resonance of the included methylene proton shifts upfield by 0.17 ppm (for proton Hα1), and another resonance of the excluded methylene proton shifts downfield by 0.06 ppm (for proton Hα2). Thus, it can be seen that the methylene protons of the Gly are in different magnetic environments, with one contained within the cavity, and the other contained within the portal, which verify that Gly and TMeQ[6] are involved in *endo*-binding modes. Further evidence for the formation of the inclusion complexes TMeQ[6]@Gly of TMeQ[6] and Gly was provided by the MALDI-TOF mass spectrometry experiment. In the ESI-MS spectra (Figure 2), the major signals atm/z = 1128.62 was observed, which corresponds to {TMeQ[6]@Gly} (calcd. 1128.018). The additional presence of Ca^{2+} was also investigated. As shown in Figure S1, on addition of TMeQ[6] to the aqueous solution of Gly, the chemical shift change of the methylene proton Hα is similar to that in Figure 1. Therefore, in the solution state, both in the presence and in the absence of Ca^{2+}, the same interaction mode between the host TMeQ[6] and guest Gly is present.

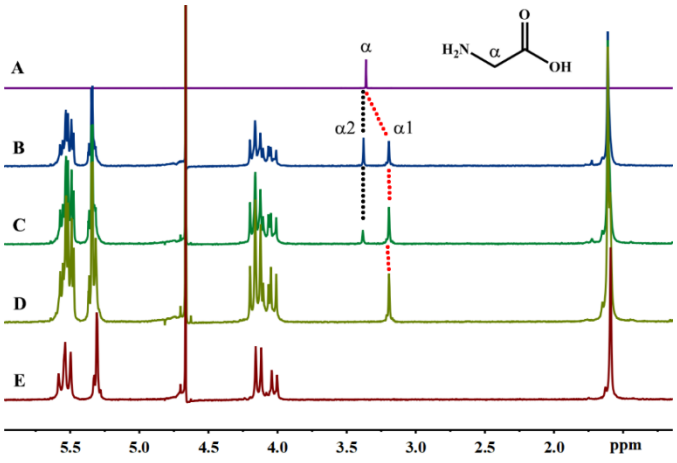

Figure 1. Interaction of Gly and TMeQ[6] (20 ℃): ^{1}H NMR spectra (400 MHz, D_2O) of (A) neat Gly, (B) in the presence of 0.5 equiv. of TMeQ[6], (C) in the presence of 0.67 equiv. of TMeQ[6], (D) in the presence of 1.0 equiv. of TMeQ[6], and (E) neat TMeQ[6].

Molecular structures

Crystals of **1** suitable for X-ray diffraction were grown from a 3M phosphoric acid solution under air over a 2 week period. Views of the molecular structure are given in Figure 3; for a view of the asymmetric unit, see Figures S2 and S3.

Complex **1** features a hydrogen-bonded dimer $(R\text{-}COOH)_2$ of two glycinium ions contained within a TMe[Q6] molecule. The NH_3^+ portions of the two molecules are located just above the opposite rims of the bowl and form hydrogen bonds to the C=O there. The structure crystallizes in the centric space group *C*2/*m* with one quarter of a TMeQ6 molecule within the asymmetric unit.

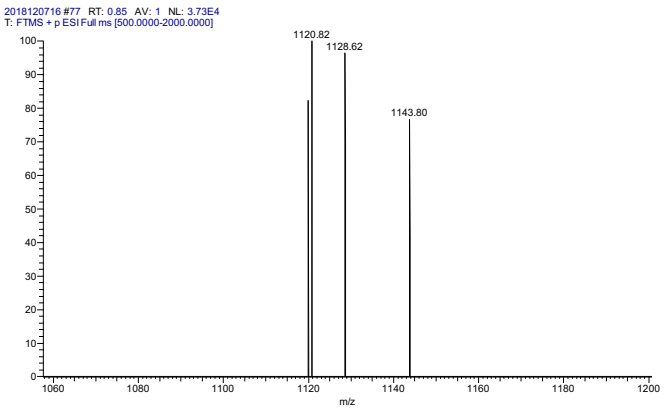

Figure 2. ESI-MS spectrum of Gly with TMeQ[6].

There is a well-determined phosphate group outside the TMeQ[6] and the oxygen atoms of water and hydronium are well-determined, but because of the relatively weak scattering we have not been able to site all of the hydrogen atoms. In common with other similar structures,[24] we have not been able to distinguish between water and hydronium. There is evidence for O-H···O hydrogen bonding between water and phosphate, TMeQ[6], and glycinium. In the case of the inclusion complex **1**, two Gly molecules are encapsulated in the hydrophobic cavity of TMeQ[6]. There are multiple non-covalent interactions between the host and guest, including O–H···O hydrogen bonds between two carboxyl groups of two encapsulated Gly molecules, and N–H···O hydrogen bonds between the amine group of the Gly and the carbonyl oxygen atoms on the TMeQ[6] portal, as well as ion–dipole interactions between the quaternized nitrogen of the Gly and the carbonyl oxygen atoms on the TMeQ[6] portal, which is is similar to that of cucurbit[6]uril with Gly previously reported[20g].

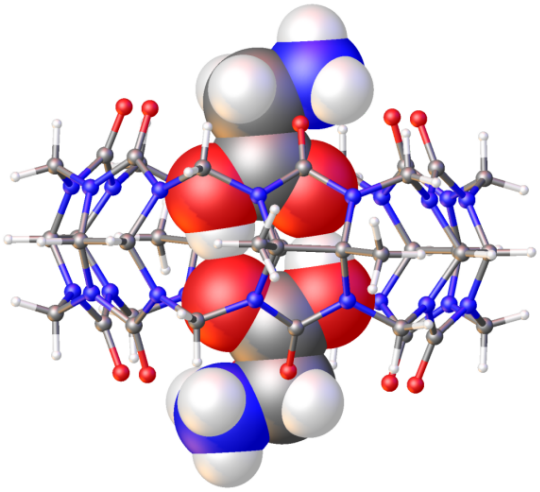

Figure 3. Hydrogen-bonded dimer of glycinium ions (space-filling representation) located with TMe[Q6] (spheres).

Crystals of complex **2** suitable for an X-ray structure determination were grown from a 3M HCl solution under air over about 1 month. Complex **2** crystallizes in the centric space group *P*-1 with a single TMeQ6 molecule in the asymmetric unit. A single calcium ion is bound, located over part of one rim of the TMeQ6 by two C=O···Ca^{2+} bonds, see Figure 4. This is also bonded to a single C=O from an adjacent TMe[Q6]. Around the calcium there are four water molecules that lie approximately in a square plane, two of which form hydrogen bonds to the rim of the bowl. A further water molecule is bound to the calcium and projects into the cavity of the first TMe[Q6] unit. This water acts as a hydrogen-bond donor to C=O of TMe[Q6]. Located at the centre of the cavity is a protonated glycine molecule and this forms a COOH···OH_2 hydrogen bond to the bound water molecule within the cavity. The -NH_3^+ group forms hydrogen bonds to C=O at the opposite rim of the TMeQ[6]. Outside of the cavity there are chloride ions that are rather poorly localised and further unbound water that was modelled using a solvent mask within the program Olex2 [27]. This gives an overall composition of TMeQ[6].$Ca(H_2O)_5$.$(Cl)_3(NH_3CH_2COOH)$.$16H_2O$.

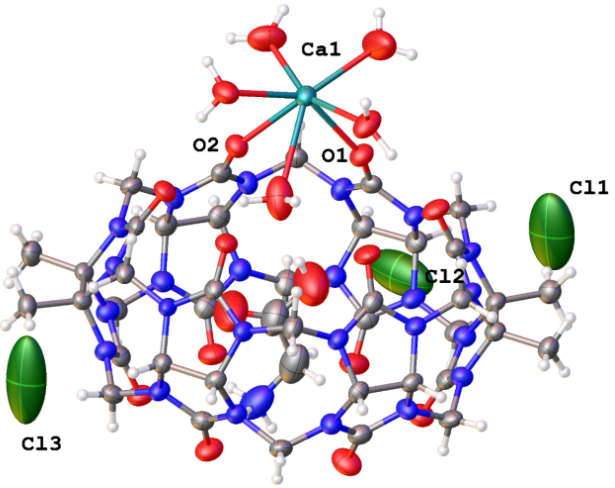

Figure 4. The asymmetric unit of complex **2**.

The presence of calcium ions linking together adjacent TMeQ[6] units gives centrosymmetric dimers that are bridged by pairs of calcium ions (Figure 5). These dumbbell-shaped units are in a simple primitive packing, which leaves space for the disordered water. From this, it is evident that in the absence of metal ions, the two glycine guests are easily encapsulated by TMeQ[6] inside the cavity to form a stable inclusion complex. In contrast, when the metal ions are added, the carbonyl oxygen of the TMeQ[6] port causes one of the ports of the TMeQ[6] to be coordinated with the metal ions, thus accommodating only one glycine guest molecule.

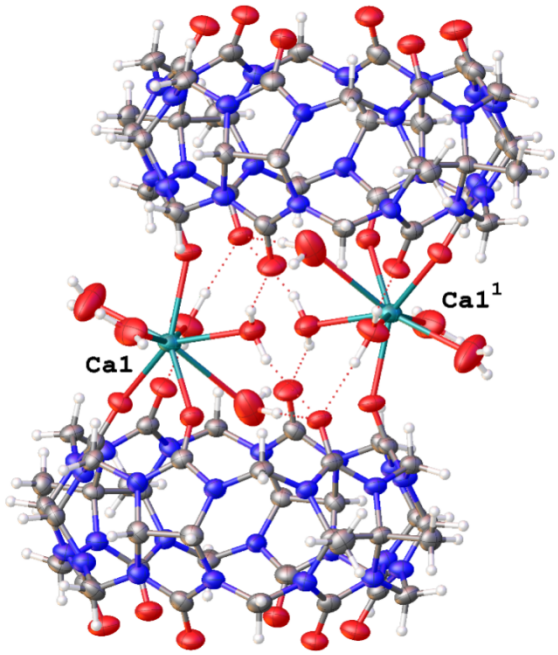

Figure 5. Dimeric assembly of two TMe[Q6] by two Ca^{2+} ions in complex **2**. Dashed lines show hydrogen bonds.

Experimental

General

TMeQ[6] was prepared in our laboratory according to a procedure in the literature.[22] All other chemicals were of analytical grade obtained from Aladdin and used as-received without further purification. All ^1H NMR data were recorded on a JNMECZ400s MHz NMR spectrometer in D_2O at 293.15 K.

Preparation of complex 1

TMeQ[6] (20.00 mg, 0.016mmol) was added to a solution of Gly (3.603 mg, 0.064 mmol) in 3M H_3PO_4 solution (3 mL). After stirring for 2 min at 60℃, the mixture was filtered. Following slow evaporation (about 2 weeks) of the filtrate under air, rhombic colorless crystals of complex **1** were afforded.

Preparation of complex 2

TMeQ[6] (20.00 mg, 0.016mmol) and $CaCl_2$ (10.65 mg, 0.096 mmol) were added to a solution of Gly (3.603 mg, 0.064 mmol)

in 3M HCl solution (3 mL). After stirring for 2 min at 60℃, the mixture was filtered. Following slow evaporation (about 4 weeks) of the filtrate under air, block colorless crystals of complex **2** were afforded. Single-crystal data for complexes **1** and **2** were collected on the Bruker Smart Apex II CCD diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. An empirical absorption correction was applied using the SADABS program.[25] All of the structures were solved with SHELXT, completed by subsequent difference Fourier syntheses, and refined on F^2 using all reflections with ShelXL-2018[26] (full-matrix least-squares techniques) in the Olex2 package.[27] All non-hydrogen atoms in the whole structure were refined with anisotropic displacement parameters. Carbon-bound hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. A solvent mask was applied for 2 within Olex2 to model the disordered solvent water molecules.[27] CCDC numbers 2192607-2192608 contain the supplementary crystallographic data for this paper.

A summary of crystal data, intensity measurements, structure solution, and refinement for **1** and **2** are given in Table S1 and below.

Crystal data for **1**. $C_{44}H_{80}N_{26}O_{34}P_2$ *Mr* = 1579.24, colourless, monoclinic, space group C2/m, *a* = 12.878(3), *b* = 20.372(5), *c* = 12.609(5), β = 106.828(6), V = 3166.3(16), Z = 2, p_{calc} = 1.652, μ(MoKα) = 0.71073, ϕ_{max} = 51.022, 57878 reflections measured, 3047 unique, parameters, *R* = 0.0394, w*R* = 0.1031 (R = 0.0556, w*R* = 0.1126). GooF = 1.042, CCDC = 2192607.

Crystal data for **2**. $C_{42}H_{92}N_{25}O_{35}CaCl_3$ *Mr* = 1653.83, colourless, triclinic, space group P-1, *a* = 13.001(4), *b* = 14.691(4), *c* = 21.030(6), α = 72.765(7), β = 76.725(7), γ = 68.800(7), V = 3542.8(18), Z = 2, p_{calc} = 1.550, μ(MoKα) = 0.71073, ϕ_{max} = 50.054, 44481 reflections measured, 12511 unique, 822 parameters, *R* = 0.0698, w*R* = 0.1809 (R = 0.0983, w*R* = 0.1972). GooF = 1.040, CCDC = 2192608.

Conclusion

In this work, we have investigated the interaction between the symmetrical tetrasubstituted cucurbit[6]uril (TMeQ[6]) and glycine, both in acidic solution and the solid-state, and with and without Ca^{2+} present. NMR spectroscopy and mass spectrometry confirm the formation of the inclusion complex TMeQ[6]@Gly; any Ca^{2+} present remains *exo* to the cavity. The product formed in the presence of phosphoric acid and in the absence of any Ca^{2+} features a hydrogen-bonded dimer $(R\text{-}COOH)_2$ of two glycinium ions contained within a TMeQ6 molecule. Conducting the reaction using HCl in the presence of $CaCl_2$ leads to the isolation of $TMeQ[6].Ca(H_2O)_5.(Cl)_3(NH_3CH_2COOH).16H_2O$, where calcium ions link together adjacent TMeQ[6] units to afford centrosymmetric dimers that are bridge by pairs of calcium ions.

Author contributions

All authors had full access to all the data in the study and take responsibility for the integrity of the data and the accuracy of the data analysis. Shang-Wei Yuan and Pei-Hui Shan have contributed equally as first authors.

Conflicts of interest

There are no conflicts to declare.

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References

[1] (a) S. L. Miller, *Science* 1953, **117**, 528-XXX; (b) K. Ruiz-Mirazo, C. Briones, A. de la Escosura, *Chem. Rev*. 2014, **114**, 285-XXX.
[2] A. G. Gale, T. T. Odbadrakh, B. T. Ball and G. C. Shields, *J. Phys. Chem*. A, 2020, **124**, 4150-XXX.
[3] A. G. Gale, T. T. Odbadrakh and G. C. Shields, *Int. J. Quantum Chem*. 2020; e26469.
[4] (a) M. Freidman, *J. Agric. Food Chem*., 1999, **47**, 3457-3479; (b) Y. Zhou and J. Yoon, *Chem. Soc. Rev*., 2012, **41**, 52-67; (c) H. Heli, M. Hajjizadeh, A. Jabbari and A. Moosavi-Movahedi, *Anal. Biochem*., 2009, **388**, 81-90; (d) Q. P. Duan, Y. Cao, Y. Li, X. Y. Hu, T. X. Xiao, C. Lin, Y. Pan and L. Y. Wang, *J. Am. Chem. Soc*., 2013, **135**, 10542-10549.
[5] (a) B. B. Shi, K. C. Jie, Y. J. Zhou, J. Zhou, D. Y. Xia and F. H. Huang, *J. Am. Chem. Soc*., 2016, **138**, 80-83; (b) G. C. Yu, G. P. Tang and F. H. Huang, *J. Mater. Chem. C*., 2014, **2**, 6609-6617; (c) G. C. Yu, D. Wu, Y. Li, Z. H. Zhang, L. Shao, J. Zhou, Q. L. Hu, G. P. Tang and F. H. Huang, *Chem. Sci*., 2016, **7**, 3017-3024.
[6] Y. Cao, X. Y. Hu, Y. Li, X. C. Zou, S. H. Xiong, C. Lin, Y. Z. Shen and L. Y. Wang, *J. Am. Chem. Soc*., 2014, **136**, 10762-10769.
[7] (a) M. Liu, J. L. Kan, Y. Q. Yao, Y. Q Zhang, B. Bian, Z. Tao, Q. J. Zhu and X. Xiao, *Sensors & Actuators: B. Chem*., 2019, **283**, 290-297; (b) R. H. Gao, L. X. Chen, K. Chen, Z. Tao and X. Xiao, *Coord. Chem. Rev*., 2017, **348**, 1-24.
[8] (a) Z. A. Wood, E. Schroder, J. R. Harris and L. B. Poole, *Trends Biochem. Sci*., 2003, **28**, 32-40; (b) Q. Zhang, D. Zhang, Y. Lu, G. Xu, Y. Yao, S. Li and Q. Liu, *Biosens. Bioelectron*., 2016, **77**, 963-970.
[9] (a) C. B. Lebrilla, *Acc. Chem. Res*., 2001, **34**, 653-661; (b) W. Si, P. Xin, Z. T. Li and J. L. Hou, *Acc. Chem. Res*., 2015, **48**, 1612-1619; (c) A. Casnati, F. Sansone and R. Ungaro, *Acc. Chem. Res*., 2003, **36**, 246-254; (d) K. Yang, Y. Pei, J. Wen and Z. Pei, *Chem. Commun*., 2016, **52**, 9316; (e) M. Giuliani, I. Morbioli, F. Sansone and A. Casnati, *Chem. Commun*., 2015, **51**, 14140; (f) R. Pinalli, A. Pedrini and E. Dalcanale, *Chem. Soc. Rev*., 2018, **47**, 7006-7026.
[10](a) A. R. Urbach and V. Ramalingam, *Isr. J. Chem*., 2011, **51**, 664; (b) A. T. Wright, M. J. Griffin, Z. L. Zhong, S. C. McCleskey, E. V. Anslyn and J. T. McDevitt, *Angew. Chem. Int. Ed*., 2005, **44**, 6375-XXX.
[11] (a) T. B. Wei, J. F. Chen, X. B. Cheng, H. Li, B. B. Han, Y. M. Zhang, H. Yao and Q. Lin, *Org. Chem. Front*., 2017, **4**, 210-XXX; (b) L. Chen, W. Si, L. Zhang, G. Tang, Z. T. Li and J. L. Hou, *J. Am. Chem. Soc*., 2013, **135**, 2152-2155; (c) S. Tashiro, M. Tominaga,

M. Kawano, B. Therrien, T. Ozeki and M. Fujita, *J. Am. Chem. Soc*., 2005, **127**, 4546-4547; (d) P. Wang, Z. T. Li and X. F. Ji, *Chem. Commun*., 2014, **50**, 13114-13116.
[12] (a) S. J. Barrow, S. Kasera, M. J. Rowland, J. del Barrio and O. A. Scherman. *Chem. Rev*. 2015, 115, 12320-12406; (b) G. Yu, K. Jie and F. Huang, *Chem. Rev*. 2015, **115**, 7240-7303; (c) H. Nie, Z. Wei, X.-L. Ni and Y. Liu, *Chem. Rev*. 2022, **122**, 9032-9077; (d) W. Zhang, Y. Luo, X.-L. Ni, Z. Tao and X Xiao, *Chem. Eng. J*. 2022, **446**, 136954; (f) W. Zhang, Y. Luo, M.-H. Jia, X.-L. Ni, Z. Tao, C.-D. Xiao and X. Xiao, *Sensor. Actuat. B-Chem*. 2022, **366**, 132006; (g)Y. Luo, W. Zhang, M. X. Yang, X. H. Feng, C. Redshaw, Q. Li, Z. Tao and X. Xiao, *Macromolecules* 2022, **55**, 1642-1646; (h) M. Liu, R. Cen, J. Li, Q. Li, Z. Tao, X. Xiao and L. Isaacs, *Angew. Chemie Int. Ed*., 2022, e202207209; (i) Y. Luo, W. Zhang, Q. Ren, Z. Tao and X. Xiao, *ACS Appl. Mater. Interfaces*, 2022, **14**, 29806 – 29812; (j) D. Yang, M. Liu, X. Xiao, Z. Tao and C. Redshaw, *Coord. Chem. Rev*., 2021, **434**, 213733; (k) Y. Luo, W. Zhang, M. Liu, J. Zhao, Y. Fan, B. Bian, Z. Tao and X. Xiao, *Chinese Chem. Lett*., 2021, 32, 367 – 370.
[13] See for example, P. H. Shan, J. H. Hu, M. Liu, Z. Tao, X. Xiao and C. Redshaw, *Coord. Chem. Rev*. 2022, **467**, 214580.
[14] A. R. Urbach and V. Ramalingam. *Isr. J. Chem*. 2011, 51, 664 – 678; (b) P. Thuéry, *CrystEngComm*, 2012, **14**, 8128–8136
[15] M. E. Bush, N. D. Bouley and A. R. Urbach, *J. Am. Chem. Soc*. 2005, **127**, 14511 – 14517.
[16] See for example, H. J. Buschmann, E. Schollmeyera and L. Mutihac. *Thermochim. Acta* 2003, **399**, 203 – 208.
[17] T. Minami, N. A. Esipenko, B. Zhang, L. Isaacs and P. Anzenbacher Jr., *Chem. Commun*. 2014, **50**, 61-63.
[18] O. Danylyuk, *CrystEngComm*, 2017, **19**, 3892–3897.
[19] K. O. Ramberg, S. Engilberge, F. Guagnini and P.B. Crowley, *Org. Biomol. Chem.*, 2021, **19**, 837–844.
[20] (a) Z.-H. Zhang, R.-L. Lin, X.-Y. Yu, L.-X. Chen, Z. Tao, X. Xiao, G. Wei, C. Redshaw and J.-X. Liu. *CrystEngComm*. 2022, **24**, 1035-1040; (b) P.-H. Shan, J.-L. Kan, X.-Y. Deng, C. Redshaw, B. Bian, Y. Fan, Z. Tao and X. Xiao, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, 2020, **233**, Article 118177; (c) Q. Bai, S. Zhang, H. Chen, T. Sun, C. Redshaw, J. -X. Zhang, X. -L. Ni, G. Wei and Z. Tao. *Chem. Select*, 2017, **2**, 2569-2573; (d) Z.-Z. Gao, J.-L. Kan, L.-X. Chen, D. Bai, H.-Y. Wang, Z. Tao and X. Xiao, *ACS Omega*, 2017, **2**, 5633-5640; (e) P. H. Shan, S. C. Tu, R. L. Lin, Z. Tao, J. X. Liu and X. Xiao. *CrystEngComm*. 2017, **19**, 2168 – 2171; (f) S. Cheng, W. Zhao, X. Yang, Y. Meng, L. Wei, Z. Tao and P. Ma, *R. Soc. Open Sci*. 2021, **8**, 202120; (g) P. Shan, R. Lin, M. Liu, Z. Tao, X. Xiao and J. Liu, *Chinese Chem. Lett*., 2021, **32**, 2301-2304; (h) P. Shan, J. Zhao, X. Deng, R. Lin, B. Bian, Z. Tao, X. Xiao, J. Liu, *Anal. Chim. Acta*, 2020, **1104**, 164-171; (i) M. Liu, R. Cen, J. Li, Q. Li, Z. Tao, X. Xiao, L. Isaacs, *Angew. Chem. Int. Edit.*, 2022, **61**, e 202207209; (j) W. Zhang, Y. Luo, J. Zhao, C. Zhang, X. Ni, Z. Tao, X. Xiao, *Chinese Chem. Lett.*, 2022, 33， 2455 – 2458.
[21] (a) J. W. Lee, H. L. Lee, Y. H. Ko, K. Kim and H. I. Kim, *J. Phys. Chem. B*. 2015, **119**, 4628–4636; (b) E. Kovalenko, M. Vilaseca, M. Díaz-Lobo, A. N. Masliy, C. Vicent and V. P. Fedin, *J. Amer. Soc. Mass Spectrom*., 2016, **27**, 265-276; (c) J. Zhang, Y.-Y. Xi, Q. Li, Q. Tang, R. Wang, Y. Huang, Z. Tao, S.-F. Xue, L. F. Lindoy and G. Wei, *Chem. Asian J.* 2016, **11**, 2250 – 2254.
[22] Y. Zhao, S. Xue, Q. Zhu, Z. Tao, J. Zhang, Z. Wei. L. Long, M. Hu, H. Xiao and A. Day, *Chin. Sci. Bull*. 2004, **49**, 1111 – 1116.
[23] See for example, W. A. Freeman, W. L. Mock and N.-Y. Shih, *J. Am. Chem. Soc*. 1981, **103**, 7367-7368.
[24] J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamguchi and K. Kim, *J. Am. Chem. Soc*. 2000, **122**, 540-541.
[25] G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.
[26] G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst*. 2015, **C71**, 3-8.
[27] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst*. 2009, **42**, 339-341.