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Shogo Amemori, Ryosuke Hamamoto and Motohiro Mizuno
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Shogo Amemori, [iD] *[abc] Ryosuke Hamamoto[d] and Motohiro Mizuno [iD] *[abc]

The association constants of various charge-transfer complexes were evaluated in *n*-hexane, octamethyltrisiloxane and PDMS to investigate the solvent effect. Higher association constants were observed in siloxanes. The association constant in PDMS increased (1.8–5.7 times) with increasing aromatic core size, implying the significant influence of aromatic cores on the solvent effect.

Charge-transfer (CT) complexes formed by the reversible inter-action between aromatic donor (π-donor) and acceptor (π-acceptor) molecules have been widely used as crucial components and driving forces in supramolecular assemblies[1–4] and organic electronic devices[5] such as organic conductors, organic photovoltaic devices, and organic field-effect transistors. In the supramolecular field, a diversity of chemical structures and high modifiability of the aromatic molecules have assisted in the development of various architectures such as molecular machines,[1] liquid crystals,[2] supramolecular gels,[3] and foldamers.[4] Because the strength of the aromatic donor–acceptor (D–A) interactions depends on the chemical structure and solvent nature, the determination of the association constants for various CT complexes can contribute to the design of supramolecular assemblies and allow the control of their properties, such as stimuli-sensitiveness and self-repair.

Many studies have investigated the solvent effects on non-covalent interaction[6] as well as CT complexes.[7] For the aromatic D–A interactions in non-polar solvents, it is generally agreed that low-polarity (weak ionization) solvents are

favorable.[7a,b,d,e] For example, Pantos *et al.* observed higher association constants for CT complexes between naphthalene-diimide derivatives and dialkoxynaphthalene derivatives in *n*-heptane than in CHCl₃.[7e] Also, it was reported that the CT complex between 1,3,5-trinitrobenzene and naphthalene has a higher association constant in *n*-heptane (9.58 M^{-1}) than in CCl₄ (5.16 M^{-1}), CS₂ (3.25 M^{-1}), and CHCl₃ (1.82 M^{-1}).[7a] However, it is difficult to provide a comprehensive explanation of the mechanisms of the gross trend in non-polar media. This is because the CT states have a weak influence on the ground state of CT complexes, indicating the complicated contributions of an electrostatic interaction, a dispersion interaction, the solvophobic effect and the CT interaction to the D–A[7b,c,f] and π–π interactions[6] among the aromatic molecules.

Poly(dimethylsiloxane) (PDMS) and oligo(dimethylsiloxane) (ODMS) are exotic non-polar media with low surface energies, weak solvation abilities, and low solubility parameters.[8] PDMS has been utilized as a lubricating and antifoaming agent and sealant in many applications. Because the siloxanes have a specific structure consisting of a flexible backbone of the siloxane bond with ionic properties and a non-polar surface of methyl side chains, they have slightly different characteristics than those of aliphatic solvents despite having a similar non-polar property. For example, PDMS and ODMS have slightly higher dielectric constants (ε_r) than aliphatic solvents. The ε_r values of PDMS, ODMS, and *n*-hexane are 2.7–2.8, 2.2–2.7, and 1.9, respectively.[9,10] Likewise, the melting points of PDMS and ODMS are lower than those of polyethylene and *n*-alkanes with analogous molecular weights. As an example, the melting points of octamethyltrisiloxane and hexadecane are −80 and 18 °C, respectively.[10]

Recently, we revealed the effect of siloxane solvents on the aromatic D–A interactions; the association constants between pyrene derivatives (**PySi** and **PyC6**) and pyromellitic diimide derivatives (**PMDISi** and **PMDIC6**) in ODMS and PDMS were three to five times higher than those in *n*-hexane, irrespective of the presence of alkyl or siloxy side chains (Fig. 1).[11] Moreover, it was shown that the enhancement by the siloxane solvent may

[a] NanoMaterials Research Institute, Kanazawa University, Kanazawa 920-1192, Japan. E-mail: amemori@staff.kanazawa-u.ac.jp, mizuno@se.kanazawa-u.ac.jp

[b] Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan

[c] Institute for Frontier Science Initiative, Kanazawa University, Kanazawa 920-1192, Japan

[d] School of Chemistry, College of Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan
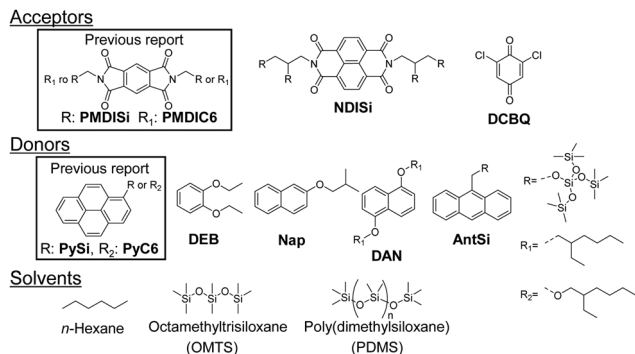
Fig. 1 Molecular structures of acceptor (**PMDISi**, **PMDIC6**, **NDISi**, **DCBQ**) and donor (**PySi**, **PyC6**, **DEB**, **Nap**, **DAN**, **AntSi**) molecules for CT complexes and solvent molecules.

originate from the incompatibility between the aromatic cores and the siloxane molecules. Meijer and co-workers also reported similar solvent effects on the complex between pyrene and naphthalenediimide derivatives in ODMS and methylcyclohexane, although the association constants of the complexes in these solvents were not evaluated.[12] It remains unclear whether the siloxane solvent effects are applicable to other CT complexes and how much the aromatic cores affect the enhancement of the association constant. The determination of the solvent effect of siloxanes will lead to the construction of supramolecular architectures in siloxane solvents by utilizing the aromatic D–A interaction as the driving force. Herein, we report the association constants of various CT complexes in octamethyltrisiloxane (OMTS) (ε_r = 2.3) as ODMS and PDMS (M_n = 2000 g mol^{-1}, ε_r = 2.7) as the siloxane solvents and n-hexane (ε_r = 1.9) as the aliphatic solvent and show the importance of the incompatibility between the aromatic core and siloxane solvents toward the aromatic D–A interaction in nonpolar solvents. Our previous report demonstrated that the siloxane solvent effect strengthened with the molecular weight of siloxanes.[11] It further predicted that the enhancement of the association constants of various CT complexes was more in PDMS than in OMTS.

To investigate the roles of the aromatic cores toward realizing the siloxane solvent effect, we chose various aromatic molecules for the CT complexes. We used **PMDISi**, 2,6-dichloro-1,4-benzoquinone (**DCBQ**), and naphthalenediimide derivatives (**NDISi**) as the acceptor molecules and **PySi**, 1,2-diethoxybenzene (**DEB**), 2-isobutoxynaphthalene (**Nap**), 1,5-dialkoxynaphthalene derivatives (**DAN**), and anthracene derivatives (**AntSi**) as the donor aromatic molecules (Fig. 1). These aromatic cores are widely utilized as the building blocks of supramolecular architectures through aromatic D–A interactions. **AntSi** and **NDISi** were synthesized by a condensation reaction between tris(trimethylsiloxy)chlorosilane and 9-anthracenemethanol or **1**, which was obtained by the reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride and 3-amino-1,2-propanediol (Scheme S1). **PMDISi, PySi** were prepared by previously reported methods.[11] Those aromatic compounds have enough solubility (>5 mM) to evaluate the

association behavior in n-hexane, OMTS and PDMS. Except for the **DCBQ-AntSi** pair, which had an unstable CT complex due to probable decomposition, the 14 combinations between the acceptor and donor molecules were evaluated for their association behavior in the three solvents. The mixing of the acceptor and donor molecules induced an increase in absorbance in the visible region originating from CT absorption in OMTS, PDMS, and n-hexane (Fig. S1, ESI†). The change in color in OMTS and PDMS upon mixing was more predominant than that in n-hexane, as confirmed by the absorption spectra and through observation by the naked eye. The significant change in absorbance in PDMS implies that all CT complexes in PDMS had higher association constants than those in other solvents.

The wavelengths of the peaks or shoulder peaks based on the CT absorptions (λ_{CT}) are listed in Table 1. The **NDISi-DEB** pair did not have an obvious absorption peak. Generally, it is known that the λ_{CT} value of CT complexes is inversely proportional to the energy gaps between the ionization energies (IE) of the donors and electron affinities (EA) of the acceptors.[7b,13] In addition to solvent properties, geometry and the distance between the donor and acceptor molecules also affect the λ_{CT} values. The **DCBQ-PySi** pair had the longest λ_{CT} wavelength and the smallest energy gap between IE and EA (ΔIE-EA), implying that **PySi** and **DCBQ** have the smallest IE and the largest EA, respectively. Significantly, there were no large spectral shifts for any of the pairs in the solvents (Fig. S2, ESI†), indicating that the complexes have similar geometries and binding models in OMTS, PDMS, and n-hexane. These results led us to compare the association constants for the solvents under consideration using the same association model.

To evaluate the association constant, K_a, the absorbance of the CT band was monitored by varying the concentration of donors at a constant acceptor concentration. The concentration dependence of absorbance was fitted through nonlinear curve fitting, and the association constants of the CT complexes were calculated (eqn (S1) and Fig. S3–S41, ESI†). The observed absorbance of CT absorption of all CT complexes in the solvents under consideration was reproduced well by the 1:1 model within the investigated concentration range; however, it may be affected by a small number of species such as 1:2 complexes and the self-assembly of the aromatics. For the same CT complexes, the values of the molar absorption coefficient (ε_{CT}) were independent of the solvents measured, supporting the same association geometries and association forms of CT complexes in these solvents (Table S1, ESI†).

The K_a values of the acceptors and donors are listed in Table 1. For the same acceptors, the optimal donor for realizing strong D–A interactions was **PySi** or **DAN**, followed by **AntSi**, **Nap**, and **DEB**. In addition, the approximate trend indicated that among the acceptors in the three solvents, the order of the K_a values with common donors was **PMDISi**, **NDISi**, and **DCBQ**. In many cases, CT complexes with a NDI core have higher association constants than those with a PMDI core.[14] The smaller K_a values of the **NDISi** systems are possibly due to the steric hindrance of the bulky side chain of **NDISi**. In fact, steric hindrance between acceptors and donors significantly affects

Table 1 Wavelength of charge-transfer absorption peaks, association constants and related parameters of the D–A pairs in n-hexane, OMTS and PDMS at 25 °C

DA pair	λ_{CT} (nm)			Association constant K_a (M⁻¹)[a]			K_a in OMTS/K_a in n-Hexane	K_a in PDMS/K_a in n-Hexane	Number of atoms	$\Delta\Delta G^\circ_{\text{hexane-OMTS}}$ (kJ mol⁻¹)	$\Delta\Delta G^\circ_{\text{hexane-PDMS}}$ (kJ mol⁻¹)
	n-Hexane	OMTS	PDMS	n-Hexane	OMTS	PDMS					
DCBQ-DEB	(450)[b]	(450)[b]	(450)[b]	1.5 (0.03)[d]	2.3 (0.06)[d]	2.7 (0.09)[d]	1.5	1.8	14	1.1	1.5
DCBQ-Nap	473	477	478	1.7 (0.02)[d]	2.9 (0.03)[d]	3.5 (0.05)[d]	1.7	2.1	18	1.3	1.8
DCBQ-DAN	553	553	554	4.5 (0.07)[d]	7.8 (0.06)[d]	8.8 (0.08)[d]	1.7	2.0	18	1.4	1.7
DCBQ-PySi	567	569	571	3.0 (0.04)[d]	5.8 (0.04)[d]	6.4 (0.10)[d]	1.9	2.1	24	1.6	1.9
PMDISi-DEB	(390)[b]	(390)[b]	(390)[b]	3.4 (0.05)[d]	5.8 (0.08)[d]	7.9 (0.10)[d]	1.7	2.3	22	1.3	2.1
PMDISi-Nap	401	401	402	5.8 (0.15)[d]	12 (0.1)[d]	17 (0.3)[d]	2.1	2.9	26	1.8	2.7
PMDISi-DAN	465	465	465	32 (0.4)[d]	84 (0.6)[d]	120 (0.8)[d]	2.6	3.8	26	2.4	3.3
PMDISi-AntSi	446	447	448	9.1 (0.21)[d]	22 (0.2)[d]	25 (0.5)[d]	2.4	2.7	30	2.2	2.5
PMDISi-PySi	468	468	470	23[e] (0.3)[d]	81[e] (1.8)[d]	130[e] (1.4)[d]	3.5	5.7	32	3.1	4.3
NDISi-DEB	—[c]	—[c]	—[c]	1.4 (0.01)[d]	2.8 (0.02)[d]	3.9 (0.06)[d]	2	2.8	26	1.7	2.5
NDISi-Nap	(450)[b]	(450)[b]	(450)[b]	2.6 (0.03)[d]	6.3 (0.04)[d]	8.5 (0.04)[d]	2.4	3.3	30	2.2	2.9
NDISi-DAN	509	507	507	9.3 (0.13)[d]	32 (0.2)[d]	51 (0.4)[d]	3.4	5.5	30	3.1	4.2
NDISi-AntSi	506	506	506	7.1 (0.05)[d]	24 (0.1)[d]	34 (0.8)[d]	3.4	4.8	34	3.0	3.9
NDISi-PySi	527	527	528	17 (0.2)[d]	63 (0.4)[d]	97 (2.5)[d]	3.7	5.7	36	3.2	4.3

[a] Association constants in three solvents were calculated using a nonlinear least squares curve fitting a 1:1 binding model. [b] Shoulder peaks. [c] An obvious peak of CT absorption was not observed. [d] Standard error for non-linear least squares in parentheses. [e] Data from ref. 11.

the stability of the complexes.[7b] For example, Foster *et al.* reported that the K_a of the CT complex between hexaethylbenzene and tetrachloro-1,4-benzoquinone (chloranil) in cyclohexane was 1.3 M⁻¹, while that of a hexamethylbenzene-chloranil pair was 28.9 M⁻¹.[15] The K_a values of the CT complexes were independent of the energy gap between the donors and acceptors (ΔIE-EA), because the K_a value of the **DCBQ-PySi** pair with the longest λ_{CT} (569 nm) was similar to that of the **PMDISi-DEB** pair with the lowest λ_{CT} (390 nm) value in OMTS. Overall, it seems that larger aromatic cores are more likely to form CT complexes with higher association constants, although there are some exceptions such as **NDISi** systems and **DAN** systems, perhaps owing to the steric effect and geometric preference among aromatic molecules for an effective HOMO–LUMO overlap.[7d,16] The relationship between the K_a values and aromatic core size suggested that the interactions among the aromatic cores dominated the aromatic D–A interactions in PDMS, OMTS and n-hexane.

Remarkably, the K_a values in OMTS and PDMS were higher than those in n-hexane for all the CT complexes. This is the first report to comprehensively reveal the universality of the siloxane solvent effect on aromatic D–A interactions using various CT complexes. The increment in the association constants, which was defined as the ratio of the K_a values in OMTS or PDMS and n-hexane, depended on the combinations of the donors and acceptors (Table 1). The association constants of **NDISi-PySi**

and **DCBQ-DEB** pairs were the most and least increased by OMTS, respectively. The tendency of enhancement was clearly observed; the complexes with larger aromatic cores were more affected by the solvent effect. To clarify the relationship between the solvent effect and core size of the aromatics, we calculated the difference of standard Gibbs free energy (ΔG°) of formation of the CT complexes between n-hexane and OMTS $\left(\Delta\Delta G^\circ_{\text{hexane-OMTS}} = \Delta G^\circ_{\text{hexane}} - \Delta G^\circ_{\text{OMTS}}\right)$. Further, we approximated the number of atoms of the aromatic cores in the CT complexes as aromatic core size (Fig. S42, ESI†). The plot of $\Delta\Delta G^\circ_{\text{hexane-OMTS}}$ *vs.* number of atoms of aromatic cores demonstrated a linear free-energy relationship (Fig. 2a), indicating the dependence of the solvent effect on the aromatic core size. Also, the solvent effect of PDMS has the linear free-energy relationship with the core size (Fig. 2b).

Generally, the boiling point and surface tension of siloxane solvents are lower than those of aliphatic solvents with similar molecular weights,[8b] indicating the occurrence of weak van der Waals interactions among the siloxane molecules. It further implies that OMTS and PDMS have lesser ability to engage in the van der Waals stabilization of flat aromatics than n-hexane, and less compatibility between the siloxanes and the aromatic molecules. Because the incompatibility is enhanced as a function of the aromatic ring size, it was supposed that the
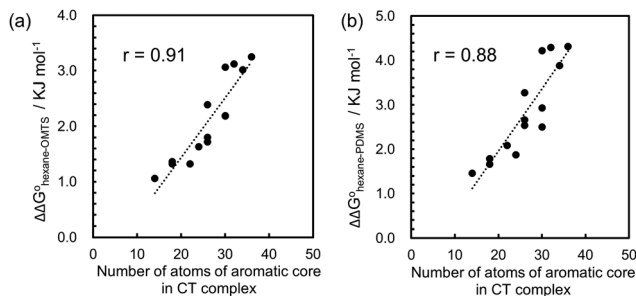
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Fig. 2 (a) Plot of $\Delta\Delta G^{\circ}_{\text{hexane-OMTS}}$ and number of atoms of aromatic core in CT complexes (correlation coefficient r = 0.91). (b) Plot of $\Delta\Delta G^{\circ}_{\text{hexane-PDMS}}$ and number of atoms of aromatic core in CT complexes (correlation coefficient r = 0.88).

enhancement of the association constant by the siloxanes increased with the increasing core size of the aromatics. Our previous report suggested that incompatibility between the aromatic core and siloxane molecules induces the siloxane solvent effect by evaluating the association constants of **PyC6-PMDIC6** in various solvents. In fact, the incompatibility between siloxane and aromatic moieties has been reportedly attributed to the phase segregation of oligo(dimethylsiloxane) with NDI moieties[17a] and of block copolymers of poly(dimethylsiloxane) and polystyrene.[17b] The results of the stronger solvent effects of the siloxanes on the CT complexes with larger aromatic molecules showed the significance of the passive force between the aromatic cores and siloxane solvents toward inducing the solvent effect.

The association constants of the 14 CT complexes with various combinations of aromatic cores in n-hexane, OMTS and PDMS were estimated. The K_a values of all complexes in the siloxane solvents were higher than those in n-hexane, although the λ_{CT} values were independent of the solvent. The universality of the solvent effect on the D–A interaction is clearly revealed for the first time. It was suggested that the solvent effect originated from the passive force between the aromatic core and siloxane, because the change in the K_a value in the solvents depended on the aromatic core size. Although the effects of steric hindrance and electric nature should also be examined using the same aromatic cores, these findings revealed that incompatibility plays a key role in the D–A interaction in non-polar solvents. Because of the lower environmental impacts of siloxane molecules than those of alkane molecules,[8d] in addition to the high association constants of various CT complexes in siloxane solvents, the CT complexes in siloxane solvents can be used to fabricate effective supramolecular systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 (a) P. Spenst and F. Würthner, *J. Photochem. Photobiol., C*, 2017, **31**, 114–138; (b) Y. Jiao, L. Đorđević, H. Mao, R. M. Young, T. Jaynes, H. Chen, Y. Qiu, K. Cai, L. Zhang, X. Y. Chen, Y. Feng, M. R. Wasielewski, S. I. Stupp and J. F. Stoddart, *J. Am. Chem. Soc.*, 2021, **143**, 8000–8010.
2 (a) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H. W. Spiess, S. D. Hudsonk and H. Duan, *Nature*, 2002, **419**, 384–387; (b) A. G. Bé, C. Tran, R. Sechrist and J. J. Reczek, *Org. Lett.*, 2015, **17**, 4834–4837; (c) M. Van Winkle, H. O. W. Wallace, N. Smith, A. T. Pomerene, M. G. Wood, B. Kaehr and J. J. Reczek, *Sci. Rep.*, 2020, **10**, 15352.
3 (a) S. Satapathy and E. Prasad, *ACS Appl. Mater. Interfaces*, 2016, **8**, 26176–26189; (b) C. Li, C. Shen, J. Nie and H. Qiu, *Chem. – Asian J.*, 2018, **13**, 1678–1682; (c) H. Zhang, J. Han, X. Jin and P. Duan, *Angew. Chem., Int. Ed.*, 2021, **60**, 4575–4580.
4 (a) R. Scott Lokey and B. L. Iverson, *Nature*, 1995, **375**, 303–305; (b) B. A. Ikkanda and B. L. Iverson, *Chem. Commun.*, 2016, **52**, 7752–7759.
5 (a) K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. Van Severen, L. Lutsen, T. J. Cleij, D. Vanderzande and J. V. Manca, *Adv. Funct. Mater.*, 2008, **18**, 2064–2070; (b) K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs and J. V. Manca, *Nat. Mater.*, 2009, **8**, 904–909; (c) W. Wang, L. Luo, P. Sheng, J. Zhang and Q. Zhang, *Chem. – Eur. J.*, 2021, **27**, 464–490.
6 (a) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525–5534; (b) Z. Chen, A. Lohr, C. R. Saha-Möller and F. Würthner, *Chem. Soc. Rev.*, 2009, **38**, 564–584; (c) C. R. Martinez and B. L. Iverson, *Chem. Sci.*, 2012, **3**, 2191–2201; (d) Z. Chen, B. Fimmel and F. Würthner, *Org. Biomol. Chem.*, 2012, **10**, 5845–5855; (e) C. Adam, L. Yang and S. L. Cockroft, *Angew. Chem., Int. Ed.*, 2015, **54**, 1164–1167; (f) L. Yang, C. Adam and S. L. Cockroft, *J. Am. Chem. Soc.*, 2015, **137**, 10084–10087; (g) R. Thakuria, N. K. Nath and B. K. Saha, *Cryst. Growth Des.*, 2019, **19**, 523–528; (h) K. Carter-Fenk and J. M. Herbert, *Chem. Sci.*, 2020, 6758–6765; (i) P. Li, E. C. Vik and K. D. Shimizu, *Acc. Chem. Res.*, 2020, **53**, 2705–2714.
7 (a) C. C. Thompson and P. A. D. de Maine, *J. Am. Chem. Soc.*, 1963, **85**, 3096–3101; (b) R. Foster, *Organic Charge-Transfer Complexes*, Academic Press Inc., London, 1969; (c) M. S. Cubberley and B. L. Iverson, *J. Am. Chem. Soc.*, 2001, **123**, 7560–7563; (d) A. Das and S. Ghosh, *Angew. Chem., Int. Ed.*, 2014, **53**, 2038–2054; (e) G. M. Prentice, S. I. Pascu, S. V. Filip, K. R. West and G. D. Pantoş, *Chem. Commun.*, 2015, **51**, 8265–8268; (f) G. Y. Lee, E. Hu, A. L. Rheingold, K. N. Houk and E. M. Sletten, *J. Org. Chem.*, 2021, **86**, 8425–8436.
8 (a) E. L. Warrick, M. J. Hunter and A. J. Barry, *Ind. Eng. Chem.*, 1952, **44**, 2196–2202; (b) M. J. Owen, *Ind. Eng. Chem. Prod. Res. Dev.*, 1980, **19**, 97–103; (c) C. Rücker and

K. Kümmerer, *Chem. Rev.*, 2015, **115**, 466–524; (*d*) M. A. Ab Rani, N. Borduas, V. Colquhoun, R. Hanley, H. Johnson, S. Larger, P. D. Lickiss, V. Llopis-Mestre, S. Luu, M. Mogstad, P. Oczipka, J. R. Sherwood, T. Welton and J. Y. Xing, *Green Chem.*, 2014, **16**, 1282–1296.

9 M. S. Beevers, S. J. Mumby, S. J. Clarson and J. A. Semlyen, *Polymer*, 1983, **24**, 1565–1570.

10 D. R. Lide, CRC Handbook of Chemistry and Physics, *A Ready-Reference Book of Chemical and Physical Data*, CRC Press, Boca Raton, FL, 90th edn, 2014.

11 S. Amemori, K. Kikuchi and M. Mizuno, *Chem. Commun.*, 2021, **57**, 1141–1144.

12 B. A. G. Lamers, M. H. C. van Son, F. V. de Graaf, B. W. L. van den Bersselaar, B. F. M. de Waal, K. Komatsu, H. Sato, T. Aida, J. A. Berrocal, A. R. A. Palmans, G. Vantomme, S. C. J. Meskers and E. W. Meijer, *Mater. Horiz.*, 2022, **9**, 294–302.

13 (*a*) R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811–824; (*b*) K. P. Castro, E. V. Bukovsky, I. V. Kuvychko, N. J. DeWeerd, Y. S. Chen, S. H. M. Deng, X. Bin Wang, A. A. Popov, S. H. Strauss and O. V. Boltalina, *Chem. – Eur. J.*, 2019, **25**, 13547–13565.

14 (*a*) Q.-Z. Zhou, M.-X. Jia, X.-B. Shao, L.-Z. Wu, X.-K. Jiang, Z.-T. Lia and G.-J. Chen, *Tetrahedron*, 2005, **61**, 7117; (*b*) S. Amemori, K. Kokado and K. Sada, *Angew. Chem., Int. Ed.*, 2013, **52**, 4174–4178.

15 R. Foster, D. Ll Hammick and B. N. Parsons, *J. Chem. Soc.*, 1956, 555–558.

16 (*a*) S. Kato, T. Matsumoto, K. Ideta, T. Shimasaki, K. Goto and T. Shinmyozu, *J. Org. Chem.*, 2006, **71**, 4723–4733; (*b*) N. S. S. Kumar, M. D. Gujrati and J. N. Wilson, *Chem. Commun.*, 2010, **46**, 5464–5466.

17 (*a*) J. A. Berrocal, R. H. Zha, B. F. M. De Waal, J. A. M. Lugger, M. Lutz and E. W. Meijer, *ACS Nano*, 2017, **11**, 3733–3741; (*b*) J. Garnier, J. Arias-Zapata, O. Marconot, S. Arnaud, S. Böhme, C. Girardot, D. Buttard and M. Zelsmann, *ACS Appl. Mater. Interfaces*, 2016, **8**, 9954–9960.