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A weaker donor shows higher oxidation state upon aggregation†

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The charge-transfer between TTFs and I₂ shows that the stronger donor TTF1 is in a cation radical state and the weaker donor TTF2 is neutral in solution, whereas TTF1 exists as a cation radical and TTF2 is dicationic in complexes. The dicationic and neutral states of TTF2 are reversible upon aggregation and solvation.

Charge-transfer (CT) between an electron donor and acceptor plays the pivotal role in supramolecular assembly and creation of conducting materials. There remains a challenge in CT, that is, whether a weaker donor could show a positively charged state higher than a stronger donor through the CT with the same acceptor.

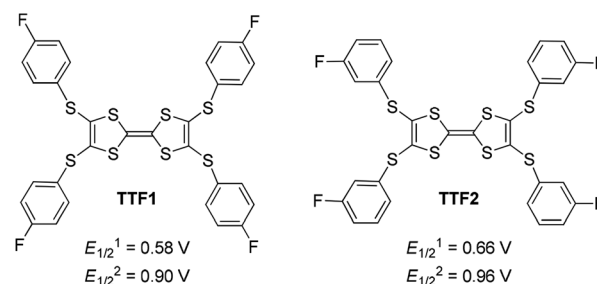
Iodine (I₂) can serve as an acceptor to prepare CT complexes. The CT complex perylene-iodine is one of the earliest organic conductors.¹ Upon gaining one electron from a donor molecule, iodine would form polyiodides,² which show diverse structures and have received growing interest in supramolecular architectures and materials science.^{3,4} Tetrathiafulvalene (TTF) is an electron donor with three reversible states, (TTF)⁰, (TTF)⁺, and (TTF)²⁺.⁵ TTF derivatives (TTFs) have been widely employed as building blocks for functional materials.⁶ The CT complexes of I₂ and TTFs can be prepared by mixing these two species.⁷ Because I₂ is not a strong acceptor, TTFs are mainly in the cation radical or partially charged state in CT complexes.⁸ Ar-S-TTFs are derived from TTF by decorating four arylthio groups onto the peripheral positions (Scheme 1). Ar-S-TTFs can adjust their geometry and electronic state to adapt to a guest molecule,⁹ and they form CT complexes with various acceptors such as fullerene,¹⁰ heteropoly acid,¹¹ and CuBr₂.¹²

The structures of polyiodides depend on the nature of the counter cations,^{3b} and Ar-S-TTFs can modulate the geometry and electronic state according to the guest. Therefore, the CT complex containing these two flexible components seems promising. Being continuous study on Ar-S-TTFs, herein we report the CT between Ar-S-TTFs (TTF1 and TTF2) and I₂. It is found that a weaker donor TTF2 carries the positive charge

higher than a stronger donor TTF1 in their CT complexes with I₂. Meanwhile, the iodine atoms form polyiodides with different structures in CT complexes, *i.e.*, the infinite covalent chain of [(I_n)⁻]_∞ in TTF2 complex and 2-D network comprised of (I₃)⁻ and I₂ in TTF1 complex.

Electrochemical analysis shows that both TTF1 and TTF2 have two reversible redox potentials. The first redox potential ($E_{1/2}^1$) of TTF2 (0.66 V vs. SCE in CH₂Cl₂) is higher than that of TTF1 (0.58 V), and the second redox potentials ($E_{1/2}^2$) show similar tendency (Scheme 1). Therefore, as donor molecule, TTF2 is weaker than TTF1. Both donors display weak absorption band at 400–500 nm due to the intramolecular CT transition,⁹ whereas the cation radicals of them show broad absorption at 650–1100 nm.¹⁴ For example, electrochemical oxidation of TTF1 under constant potential of 0.75 V results in an absorption band in this region as proved by the spectroelectrochemical study (Fig. 1a).

By mixing TTF1 and I₂ in CH₂Cl₂, an absorption band appears at 650–1100 nm (Fig. 1b), which is identical to that observed in the spectroelectrochemistry. The mixture of TTF1 and I₂ in CH₂Cl₂ shows ESR signal with $g = 2.006$ (Fig. 1c). Therefore, the CT occurs between TTF1 and I₂ in CH₂Cl₂ solution, and TTF1 is at the cation radical state. While CT occurs between TTF1 and I₂ in CH₂Cl₂, the thin layer chromatography reveals that the neutral TTF1 remains in solution even though excess I₂ is added (>3 equiv.); this means I₂ cannot completely



Scheme 1 Chemical structures of the Ar-S-TTFs reported herein, along with their first ($E_{1/2}^1$) and second ($E_{1/2}^2$) redox potentials in CH₂Cl₂ recorded *versus* SCE.

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† Electronic supplementary information (ESI) available: CCDC 1818732 and 1818736 respectively for (TTF1)·(I₃)·(I₂) and (TTF2)·(I₅)·(I₂) contain the crystallographic data. The selected crystallographic data are supplied in Table S1 in ESI. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ra02956c



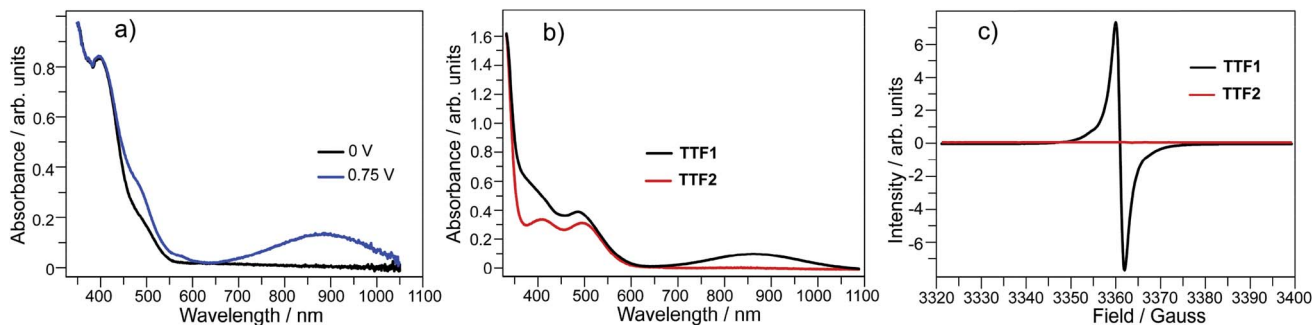


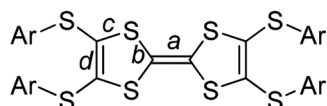
Fig. 1 (a) Spectroelectrochemistry of **TTF1** in CH_2Cl_2 ($c = 5 \times 10^{-4} \text{ mol L}^{-1}$); (b) UV-Vis absorption spectra and (c) ESR spectra of **TTF1** and **TTF2** upon adding 3 equivalents of I_2 in CH_2Cl_2 ($c = 1 \times 10^{-5} \text{ mol L}^{-1}$).

transform **TTF1** into cation radical. On the other hand, there is no CT between **TTF2** and I_2 in CH_2Cl_2 solution, because the absorbance of $(\text{TTF2})^{2+}$ is not observed (Fig. 1b) and the mixture of **TTF2** and I_2 is ESR inactive (Fig. 1c).

Although **TTF1** and **TTF2** exhibit the different behaviors upon mixing with I_2 in CH_2Cl_2 , they both afford CT complexes with I_2 . The CT complexes are obtained as black block-like single crystals by evaporating the $\text{CH}_2\text{Cl}_2/n$ -hexane (v/v , 1 : 1) solution of mixture of **TTF1** (or **TTF2**) and I_2 at room temperature. The compositions of complexes are determined on the basis of single crystal structure analyses to be $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ and $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$.

$(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ crystallizes in the $P\bar{1}$ space group. There are one **TTF1** molecule and three pairs of iodine atoms (I1–I2, I3–I4, and I5–I6) in the asymmetric unit. The I3 and I5 locate on the inversion centres. The bond length of central C=C (bond *a* in Scheme 2) on TTF moiety can be used to estimate the charge on TTFs,⁷ *i.e.*, 1.34 Å, 1.39 Å, and 1.45 Å respectively for $(\text{TTF})^0$, $(\text{TTF})^+$, and $(\text{TTF})^{2+}$. Referring Fig. 2a, the central C=C bond length in **TTF1** is 1.39 Å, same to that in $(\text{TTF})^+$.⁷ The site charge (ρ) on TTF moiety also can be estimated *via* an empirical formula $\rho = 6.347 - 7.436\delta$,¹³ where $\delta = (b + c) - (a + d)$, and *a*, *b*, *c*, and *d* are bond lengths (Scheme 2). The calculated δ -value of **TTF1** is 0.721 Å, which gives the site charge on **TTF1** to be +1. The iodine atoms (I1–I6) form three tightly connected units, [I1–I2], [I4–I3–I4], and [I6–I5–I6] (Fig. 2c). The I1–I2 bond length (2.74 Å) is identical to that of neutral I_2 (2.74 Å), and the I–I bond lengths (2.91–2.93 Å) in both [I4–I3–I4] and [I6–I5–I6] are very close to that of triiodide (2.90 Å).¹⁴ Therefore, the [I4–I3–I4] and [I6–I5–I6] units are intrinsic $(\text{I}_3)^-$. These results indicate that **TTF1** is at cation radical state in complex, which is reasonable according to the formation of $(\text{TTF1})^+$ in solution by mixing **TTF1** and I_2 .

The **TTF1** molecules are dimerized in complex (Fig. 2b). Within a dimer, there are S⋯S contacts (3.45–3.53 Å) between TTF cores, and C⋯S contacts (3.42–3.46 Å) between the



Scheme 2 The bonds (*a*–*d*) on Ar-S-TTFs for the estimation of charge ρ .

peripheral sulfur atoms and the phenyls. Meanwhile, the $(\text{I}_3)^-$ anions and neutral I_2 together form the two-dimensional (2-D) sheet *via* multiple I⋯I contacts (3.32–3.96 Å). The 2-D sheet is not flat but shows a zig-zag shape along the *b*-axis direction (Fig. 2d). The dimers of **TTF1** are sandwiched by the neighbouring 2-D anion sheets. There are I⋯S contacts (3.69–3.78 Å) between the anion sheets and **TTF1** dimers. This type of 2-D polyiodide framework is rare in the CT complexes of TTFs and I_2 .¹⁵

$(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ crystallizes in the $C2/c$ space group. The asymmetric unit contains half of **TTF2**, three tightly connected iodine atoms (I1, I2, I3) with I3 on the 2-fold screw axis, and one isolated iodine atom (I4) at the general position. Referring Fig. 3a, the central C=C bond length (1.45 Å) on TTF moiety is close to that observed in the dicationic salts of Ar-S-TTFs (1.42 Å).¹² The calculated δ value of **TTF2** is 0.573 Å, giving the site charge on **TTF2** to be +2. These results firmly prove that **TTF2** is dicationic in complex, against the neutral state of **TTF2** by mixing it with I_2 in CH_2Cl_2 . As shown in Fig. 3b, the I4–I4 bond length (2.79 Å) is close to that of I_2 (2.73 Å), thus the $(\text{I4})_2$ is a neutral I_2 . The I1, I2, and I3 atoms form an infinite chain with a periodicity of $-\text{[I1-I2-I3-I2-I1]}-$. Regarding the charge on **TTF2**, a periodic unit [I1–I2–I3–I2–I1] has a charge of -2 . The interatomic distances in [I1–I2–I3–I2–I1] unit vary from 3.04 Å to 3.19 Å, almost identical to those in the infinite polymeric $[(\text{I}_n)^-]_\infty$ (3.02–3.20 Å).^{3a} Therefore, the present polyiodide chain also would be a $[(\text{I}_n)^-]_\infty$ polymer, and all the iodine atoms in $[(\text{I}_n)^-]_\infty$ are partially charged.^{3a} The $[(\text{I}_n)^-]_\infty$ chains are connected by $(\text{I4})_2$ through the I⋯I contacts (3.42 Å) to form a ladder-like structure. The TTF cores and peripheral aryls on **TTF2** molecules together form a channel along the longitudinal axis of **TTF2** (Fig. 3c), and the channel grows through the C⋯S contacts (3.34–3.48 Å) between the peripheral sulfur atoms and the phenyls. The $[(\text{I}_n)^-]_\infty$ chains penetrate into the channel. It is worth noting that $[(\text{I}_n)^-]_\infty$ chain has not been observed in the complexes comprised of TTFs and polyiodide.

The charged states of **TTF1**/**TTF2** in CT complexes are further proved by the spectroscopic studies. $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ shows a ESR signal with $g = 2.009$ and $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ is ESR inactive (Fig. 4a). This is consistent with crystallographic study, *i.e.*, **TTF1** and **TTF2** are respectively at cation radical and dicationic states. The UV-Vis absorption spectra of both complexes in solid state are distinct from those of neutral **TTF1** and **TTF2** (Fig. 4b). $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ shows two absorption bands at the low energy

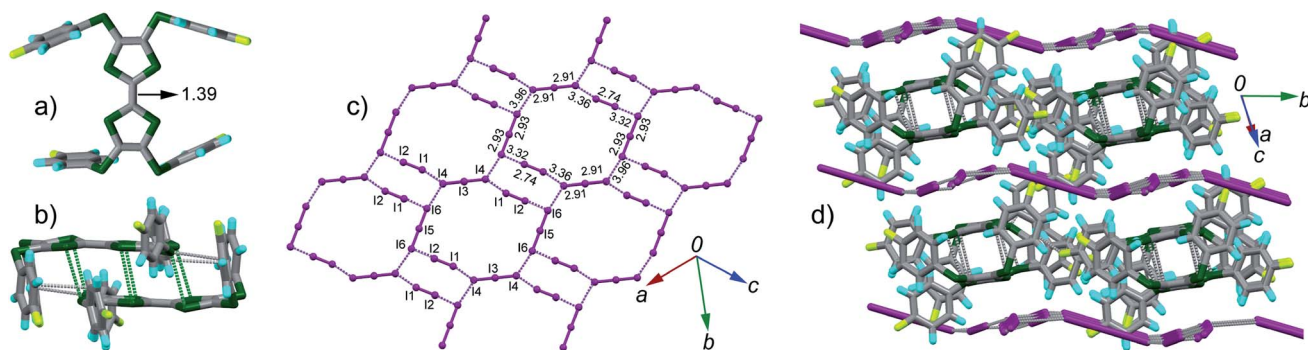


Fig. 2 Crystal structure of complex $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$: (a) top view of molecule **TTF1** with the central $\text{C}=\text{C}$ bond length shown in unit of Å; (b) **TTF1** dimer with atomic short contacts shown in dashed lines (green for $\text{S} \cdots \text{S}$ and grey for $\text{C} \cdots \text{S}$); (c) anion sheets composed of $(\text{I}_3)^-$ and I_2 with the $\text{I}-\text{I}$ bond length and $\text{I} \cdots \text{I}$ contacts (purple dashed lines) shown; (d) packing structure viewed along the longitudinal axis of **TTF1** dimer with the $\text{I} \cdots \text{I}$ contacts shown in grey dashed lines.

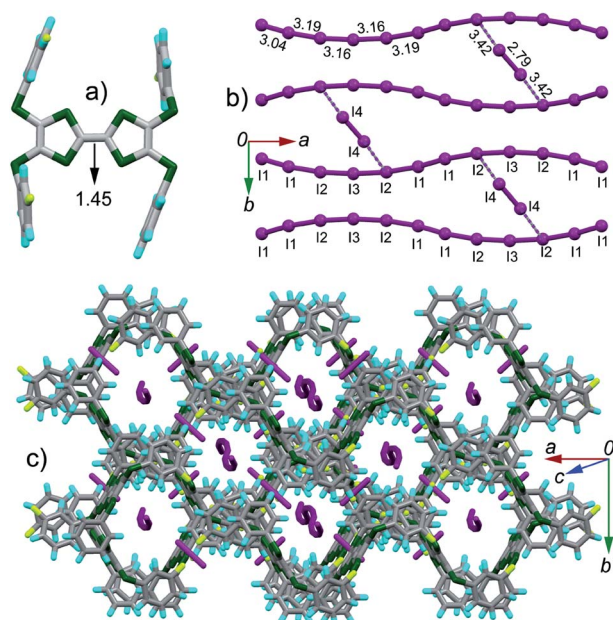


Fig. 3 Crystal structures of complex $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$: (a) top view of molecule **TTF2** with the central $\text{C}=\text{C}$ bond length shown in unit of Å; (b) the $(\text{I}_5)^-$ anion chain with the $\text{I}-\text{I}$ bond lengths and $\text{I} \cdots \text{I}$ contacts (purple dashed lines) shown; (c) packing structure projected along the longitudinal axis of the **TTF** moiety.

region. The band at 800–950 nm that belonging to absorbance of $(\text{TTF1})^{+\bullet}$. The band at 950–1400 nm ascribable to intermolecular CT transition between the **TTF1** cation radicals in a dimer, *i.e.*, $(\text{TTF1})^{+\bullet} + (\text{TTF1})^{+\bullet} \rightarrow (\text{TTF1})^{2+} + (\text{TTF1})^0$.^{8a} The $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ displays very broad absorption at 500–1400 nm, which is distinct from $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$.

As aforementioned, **TTF2** is neutral upon mixing with I_2 in CH_2Cl_2 , whereas it is dicationic in $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$. Moreover, **TTF2** is a donor weaker than **TTF1**, but it shows higher oxidation state in complex. This is against to the criteria for CT between **TTF** and acceptor, say, the charge on **TTF** in CT complex depends on the oxidation potential (E_{D}^{ox}) of **TTF** and the reduction potential ($E_{\text{A}}^{\text{red}}$) of acceptor.¹⁶ The **TTF** would be neutral, cation radical, and partially charged under the condition of $E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} > 0.34$ V, $E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} < -0.02$ V, and -0.02 V $< E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} < 0.34$ V, respectively. In the present case, the $E_{\text{A}}^{\text{red}}$ of **TTF2** is 0.69 V and the $E_{\text{A}}^{\text{red}}$ of I_2 is 0.53 V (Fig. S4 in ESI†). Therefore, **TTF2** would be partially charged in CT complex. One may concern that the increment of charge transfer degree between I_2 and **TTF2** in $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ would be attributed to the aggregation of donor and acceptor.

In this regard, the absorption spectra of complexes are studied by dissolving them in CH_2Cl_2 . $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ shows characteristic absorbance of $(\text{TTF1})^{+\bullet}$ in CH_2Cl_2 (Fig. 4c), therefore the charged state of **TTF1** remain the same in solution and CT complex. On the other hand, the charge on **TTF2** is distinctly varied by dissolving $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ in CH_2Cl_2 . The **TTF2** is

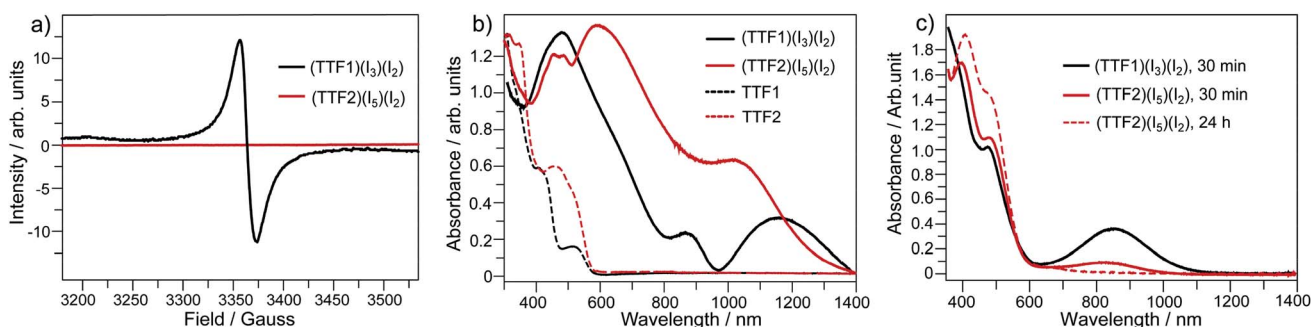
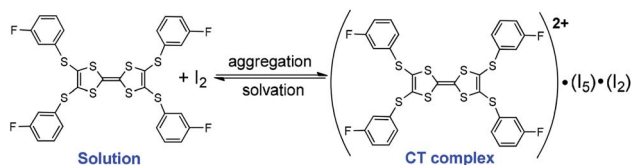


Fig. 4 (a) ESR spectra for the crystalline complexes of $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ and $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$; UV-Vis absorption spectra of $(\text{TTF1}) \cdot (\text{I}_3) \cdot (\text{I}_2)$ and $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ in the (b) solid state, and (c) CH_2Cl_2 solution ($c = 10^{-5} \text{ mol L}^{-1}$) after standing under inert atmosphere for 30 min and/or 24 h.



Scheme 3 Reversible process upon aggregation and solvation of $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$

reduced from $(\text{TTF2})^{2+}$ to $(\text{TTF2})^{+}$ in 30 min as proved by an absorption band at 700–1050 nm. And, the $(\text{TTF2})^{+}$ disappears to give neutral **TTF2** when the solution is kept for 24 h under inert atmosphere. This means that the retro CT occurs from $[(\text{I}_n)^-]_\infty$ to $(\text{TTF2})^{2+}$ upon dissociation of $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$, and both anionic and cationic components return to the neutral state. Moreover, the absorbance of $(\text{TTF2}) \cdot (\text{I}_5) \cdot (\text{I}_2)$ can be restored by evaporating the solution to gain solid complex. This process, exchanging the dicationic and neutral states of **TTF2**, is thus reversible upon aggregation and solvation of complex as shown in Scheme 3. These results prove that the dicationic state of **TTF2** in CT complex comes from the aggregation of donor and acceptor.

In summary, the CT between **TTF1/TTF2** and I_2 is studied in both solution and solid state. The stronger donor **TTF1** turns into cation radical and the weaker donor **TTF2** remains neutral upon mixing with I_2 in solution. On the other hand, **TTF2** shows an oxidation state (dicationic) higher than that of **TTF1** (cation radical) in their CT complexes, which is unusual for CT between TTFs and acceptors. The high oxidation state of **TTF2** in complex is due to the aggregation of donor and acceptor. The dicationic and neutral states of **TTF2** are reversible upon aggregation and solvation of CT complex. Moreover, the structures of polyiodides in CT complexes can be finely tuned by varying the aryls on Ar-S-TTFs, to give infinite $[(\text{I}_n)^-]_\infty$ and 2-D network comprised of $(\text{I}_3)^-$ and I_2 . Along with previous report, this work further indicates that Ar-S-TTFs show unique feature, *i.e.*, self-modulation of electronic states and molecular geometries according to guest molecules.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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