



Metalla-Assembled Electron-Rich Tweezers: Redox-Controlled Guest Release Through Supramolecular Dimerization

Serhii Krykun, Maksym Dekhtiarenko, David Canevet, Vincent Carré,
Frédéric Aubriet, Eric Levillain, Magali Allain, Zoia Voitenko, Marc Sallé,
Sébastien Goeb

► To cite this version:

Serhii Krykun, Maksym Dekhtiarenko, David Canevet, Vincent Carré, Frédéric Aubriet, et al.. Metalla-Assembled Electron-Rich Tweezers: Redox-Controlled Guest Release Through Supramolecular Dimerization. *Angewandte Chemie International Edition*, Wiley-VCH Verlag, 2020, 59 (2), pp.716-720. 10.1002/anie.201912016 . hal-02390513

HAL Id: hal-02390513

<https://hal.archives-ouvertes.fr/hal-02390513>

Submitted on 7 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Metalla-Assembled Electron-Rich Tweezers: Original Redox-Controlled Guest Release through Supramolecular Dimerization

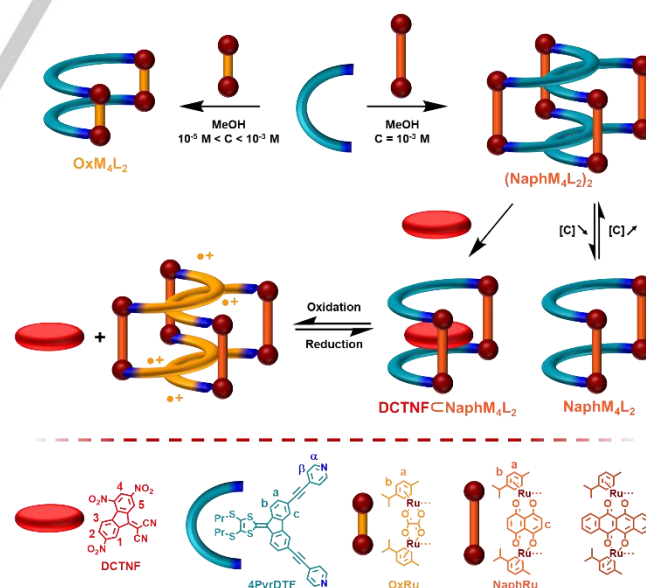
Serhii Kryhun,^{[a],[b]} Maksym Dekhtiarenko,^{[a],[b]} David Canevet,^[a] Vincent Carré,^[c] Frédéric Aubriet,^[c] Eric Levillain,^[a] Magali Allain,^[a] Zoia Voitenko,^[b] Marc Sallé^[a] and Sébastien Goeb^{*,[a]}

Abstract: Developing methodologies to control on demand the release of a molecular guest requires the rational design of stimuli-responsive hosts bearing functional cavities. While a substantial number of responsive metalla-cages have been described so far, the case of coordination-tweezers has been less explored. Herein, we report the first example of a redox-triggered guest release from a metalla-assembled tweezer. The latter incorporates two redox-active panels facing each other and constructed from the electron-rich 9-(1,3-dithiol-2-ylidene)fluorene unit. The tweezer dimerizes spontaneously in solution and the resulting interpenetrated supramolecular structure is able to dissociate in presence of an electron-poor planar unit, forming a 1:1 host-guest complex. The latter can be dissociated upon tweezer oxidation/dimerization, offering an original redox-triggered molecular delivery pathway.

Designing functional supramolecular materials requires a fine control over the relative spatial organization and stoichiometry of the constitutive elements. The coordination driven self-assembly methodology may lead to highly predictable geometries, by using complementary metal complexes and organic ligands. For instance, this strategy has been used to produce discrete supramolecular structures in very high yields.^[1] In particular, important efforts have been devoted to devise molecular hosts in order to target applications such as drug delivery,^[2] catalysis,^[1b, 3] or sequestration of pollutants/reactive molecules.^[3a] A step further has been reached with the design of functional cavities able to release on-demand an encapsulated guest, in response to an external stimulus.^[4] In the course of our recent investigations in designing functional redox-active rings and cages^[5] inspired from the tetrathiafulvalene (TTF) framework,^[6] we recently depicted a redox-triggered guest releasing from electron-rich coordination cages.^[7]

Beside the widely described family of coordination rings and cages, i.e. featuring a closed cavity, molecular tweezers constitute a class of acyclic host molecules prone to bind various guest systems.^[8] In this case, the cavity is geometrically defined by two panels facing each other and maintained in a more or less parallel conformation by a linker. Their guest binding capacities depend on the inherent properties (e.g. electronic) of their panels and on the distance separating them. For instance, a distance of ca. 7 Å is considered to facilitate the binding of a planar aromatic molecule, the resulting host-guest system being possibly stabilized in this case through π - π , CH- π or donor-acceptor non-covalent interactions. Some molecular tweezers constructed from the electron-rich tetrathiafulvalene family have already been described,^[9] but none has been constructed from the coordination-driven self-assembly strategy to our knowledge, though the latter has been extensively used to reach various supramolecular objects.^[1b, 10]

We report herein the one-pot synthesis of two ruthenium-based self-assembled molecular tweezers **OxM₄L₂** and **NaphM₄L₂** featuring the electron-rich 9-(1,3-dithiol-2-ylidene)fluorene unit. These complexes differ by the respective distances separating both dithiafulvenyl (DTF) tips, a parameter which is tuned depending on the length of the bis-ruthenium complex spacer



[a] Dr. S. Krykun, M. Dekhtiarenko, Dr. D. Canevet, Dr. E. Levillain, M. Allain, Dr. S. Goeb, Prof. M. Sallé
Laboratoire MOLTECH-Anjou, UMR CNRS 6200, UNIV Angers,
SFR MATRIX, 2 Bd Lavoisier, 49045 Angers Cedex, France.
E-mails: marc.salle@univ-angers.fr; sebastien.goeb@univ-angers.fr

[b] Prof. Z. Voitenko
Taras Shevchenko National University of Kyiv, 64/13
Volodymyrska st., Kyiv 01033, Ukraine

[c] Dr. V. Carré, Prof. F. Aubriet,
LCP-A2MC, FR 3624, Université de Lorraine, ICPM
1 Bd Arago, 57078 Metz Cedex 03, France

Supporting information for this article is given via a link at the end of the document.

Figure 1. Synthesis of self-assembled tweezers **oxM₄L₂** and **(NaphM₄L₂)₂** from ligand **4PyrDTF** and complexes **OxRu** and **NaphRu** respectively, and supramolecular transformations occurring from **(NaphM₄L₂)₂**.

COMMUNICATION

(**OxRu** or **NaphRu**) (Figure 1). Whereas the smaller tweezer (**OxM₄L₂**) is observed as an individual unit, the larger one spontaneously forms the interpenetrated supramolecular dimer (**NaphM₄L₂**)₂ in solution and in the solid state. This dimer can be dissociated either upon dilution to $C < 10^{-3}$ M, or upon addition of an electron-poor aromatic guest (i.e. 9-dicyanomethylene-2,4,7-trinitrofluorene (DCTNF)), affording the **NaphM₄L₂** monomer or the DCTNF⊂**NaphM₄L₂** host guest complex respectively. Remarkably, the latter can be reversibly shifted to a tweezer dimer upon oxidation, with concomitant guest release (Figure 1).

The synthesis of tweezer **OxM₄L₂** was achieved in one-step from a stoichiometric mixture of redox active ligand **4PyrDTF**^[11] and arene ruthenium acceptor **OxRu**^[12] in MeOH at $C = 10^{-3}$ M (15 h, 50°C). After precipitation with Et₂O, the resulting solid exhibits a ¹H NMR spectrum (MeOD) with α/β pyridyl and fluorenyl signals upfield shifted in comparison with starting **4PyrDTF**, as a result of the metal-ligand coordination (Figure 2a-b). A ¹H NMR DOSY experiment (Figure S5) revealed the presence of only one discrete species in solution with a diffusion coefficient (*D*) of 3.31×10^{-10} m² s⁻¹ in MeOD at $C = 10^{-3}$ M. The corresponding calculated Stokes radius of 12 Å, is in good agreement with the formation of the expected M₄L₂ species.^[13] Interestingly, the ¹H NMR spectrum (MeOD) obtained from the reaction of **4PyrDTF** with the **NaphRu**^[14] acceptor (Figure 2c), shows a splitting of each signal, indicating the possible formation of a dimer structure. In particular, the large upfield shifts of fluorenyl aromatic protons (a-c) in the 5.5–7.0 ppm region suggests an association driven by π - π interactions. The formation of a dimeric structure is further confirmed by the Stokes radius of 19 Å calculated from a ¹H DOSY NMR experiment (Figure S8), a value which is significantly larger than the one observed with **OxRu**. One will note that no discrete structure could be reached from the larger **TetraRu** acceptor.^[14]

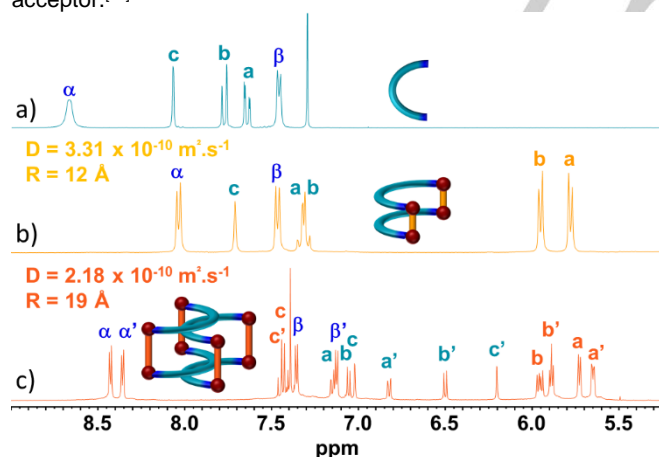


Figure 2. ¹H NMR (298 K, $C = 10^{-3}$ M, downfield region) of a) ligand **4PyrDTF** in CDCl₃, b) **OxM₄L₂** in MeOD and c) (**NaphM₄L₂**)₂ in MeOD. See Figure 1 for ¹H NMR assignments. *D* corresponds to the diffusion coefficient extracted from a ¹H DOSY NMR experiment and *R* to the corresponding hydrodynamic radii calculated from the Stokes-Einstein equation.

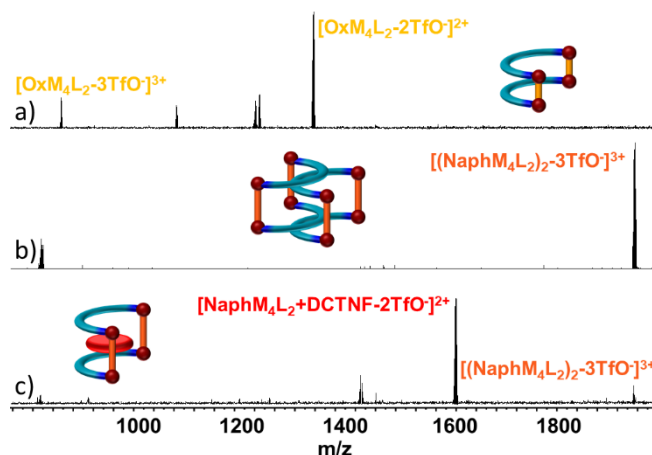


Figure 3. ESI-FTICR mass spectra recorded in CH₃CN at $C = 10^{-3}$ M of a) **OxM₄L₂**, b) (**NaphM₄L₂**)₂ and c) (**NaphM₄L₂**)₂ with 2 equiv. of DCTNF.

High-resolution ESI-FTICR-MS spectrometry experiments were carried out on the isolated **OxM₄L₂** and (**NaphM₄L₂**)₂ self-assembled complexes in CH₃CN at $C = 10^{-3}$ M (Figure 3 and Figures S15, S16). While the metalla-tweezer obtained from **OxRu** exhibits only signals resulting from the monomeric **OxM₄L₂** species at $m/z = 1325.0751$ and 833.3996 (main contributions, Figure 3a), the self-assembly isolated from the reaction between **4PyrDTF** and the larger **NaphRu** acceptor shows one isotopic pattern at $m/z = 1949.4623$ corresponding to the dimeric (**NaphM₄L₂**)₂ species (main contribution, Figure 3b). It is worth noting that no signal corresponding to the monomeric tweezer is observed, highlighting the stability of the supramolecular dimer, even in the gas phase. Eventually, all experimental isotopic distributions are in good agreement with calculated theoretical ones (Figures S15 and S16).

Single crystals suitable for X-ray diffraction analyses were obtained for both ruthenium-based tweezers, by liquid diffusion of methyl *tert*-butyl ether into a solution of the self-assembled structures in methanol at room temperature (Figure 4). The

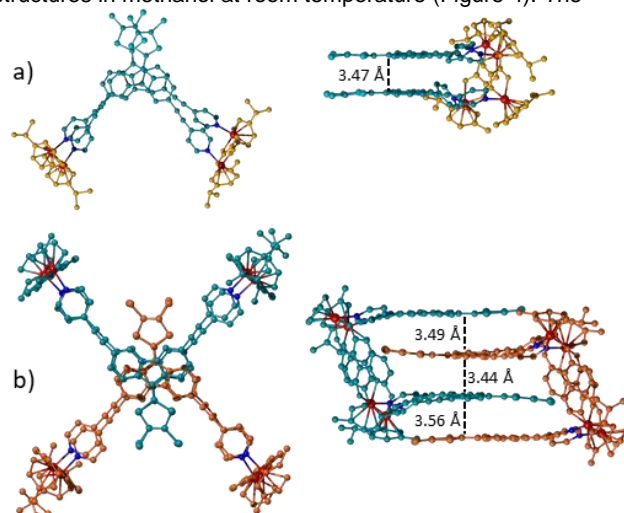


Figure 4. X-Ray crystal structures of a) **OxM₄L₂** and b) (**NaphM₄L₂**)₂. Propyl chains have been omitted for clarity.

monomeric structure of **OxM₄L₂** consists in two DTF electro-active units facing each other thanks to π - π interactions, with a distance of 3.47(1) Å (Figure 4a). Consequently, both **OxRu** spacers, in which the ruthenium atoms are separated by 5.49(1) Å, are twisted by 19.55 and 32.65° respectively from the ideal perpendicular conformation with the dithiafulvenyl fragments (Figure S20). The X-ray crystal structure of **(NaphM₄L₂)₂** reveals that two metalla-tweezers are partially stacked and stabilized by intermolecular π - π interactions with distances in the range of 3.44-3.56(1) Å (Figure 4b). No additional stabilization forces such as CH- π interactions between the DTF ligands and the hydroxy-naphthoquinonato units are observed, while these have been described as the main driving forces for interlocking carbazole-based ligands.^[15]

The stability of the dimer arrangement has been investigated by performing variable-concentration NMR experiments in deuterated methanol at 298 K (Figures 5a-c and S10). Diluting the solution from $C = 10^{-3}$ M to $C = 3 \times 10^{-5}$ M results in a drastic simplification of the NMR spectrum and to the disappearance of all signals in the 6–7 ppm region. Dissociation of the dimer is further supported by a ^1H DOSY NMR experiment recorded at $C = 3 \times 10^{-5}$ M from which a diffusion coefficient $D = 3.63 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ has been extracted (Figure S11), a value similar to that observed for the monomer **OxM₄L₂** tweezer ($D = 3.31 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, Figure 2 and S5). The slow equilibrium between the monomer and the dimer species at the NMR timescale, allowed a straightforward determination of the dimerization constant $K_{\text{dim}}(\text{MeOD}) = 4416 \pm 246$ (Figure S12).^[16] In order to study further the stability of the dimeric **(NaphM₄L₂)₂** species, we investigated its behavior in presence of DCTNF, such electron-poor unit being known to interact strongly with electron-rich derivatives.^[17] Interestingly, upon addition of 4 equivalents of

DCTNF into a solution of **(NaphM₄L₂)₂** ($C = 10^{-3}$ M, MeOD), the ^1H NMR spectrum appeared significantly simplified (Figure 5d), illustrating the dissociation of the dimeric species. Moreover, the resulting α and β protons show chemical shifts similar to those of the **NaphM₄L₂** monomer (Figure 5c), while signals corresponding to the DTF core are upfield shifted. Such observation suggests the intercalation of the electron-poor DCTNF plan between both DTF tips of the **NaphM₄L₂** monomer. A ^1H NMR DOSY experiment from which diffusion coefficients of $3.07 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ and $3.73 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ could be extracted for the host and the guest respectively (Figure 5d and Figure S15) confirms *i*) the drastic decreasing of the self-assembly radius size, which is now comparable to the one of **NaphM₄L₂** monomer and *ii*) the strong host-guest interaction. Finally, the formation of the **DCTNF ⊂ NaphM₄L₂** complex is unambiguously demonstrated by an ESI-FTICR mass analysis of a mixture of **(NaphM₄L₂)₂** and 2 equivalents of DCTNF in acetonitrile, for which a characteristic

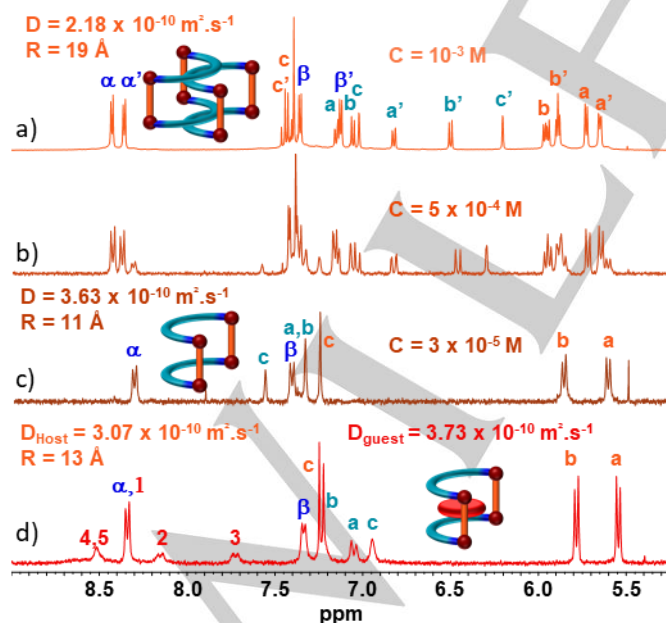


Figure 5. a-c) ^1H NMR spectra evolution in MeOD of **(NaphM₄L₂)₂** from $C = 10^{-3}$ M to $C = 3 \times 10^{-5}$ M and d) ^1H NMR spectrum recorded from a solution at $C = 10^{-3}$ M of **(NaphM₄L₂)₂** containing 4 equiv. of DCTNF.

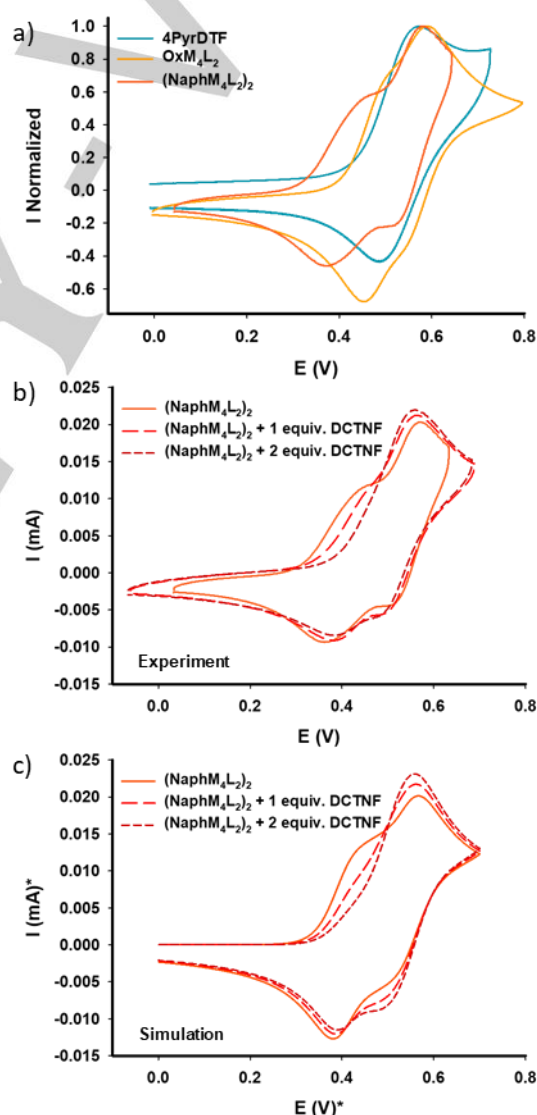


Figure 6. Cyclic voltammogram at $C = 10^{-3}$ M in 0.1 M TBAPF₆ (CH₃CN, 100 mV.s⁻¹, vs Fc/Fc⁺) of a) **4PyrDTF**, **OxM₄L₂** and **(NaphM₄L₂)₂** in presence of **DCTNF**; c) Simulated Cyclic voltammogram of **(NaphM₄L₂)₂** in presence of **DCTNF**.

signal of the doubly charged species is found at $m/z = 1606.6168$ (Figure 3c and S17).

The electrochemical properties of both **OxM₄L₂** monomer and **(NaphM₄L₂)₂** dimer were studied by cyclic voltammetry in CH₃CN at $C = 10^{-3}$ M and compared to those of ligand **4pyrDTF** (Figure 6a). The latter exhibits one reversible oxidation wave at $E_{1^{ox}} = 0.56$ V vs Fc/Fc⁺ that is ascribed to the formation of a radical cation.^[18] This value is in good accordance with the one reported for the analogous SHexyl functionalized ligand.^[11] Interestingly, both self-assembled structures **OxM₄L₂** and **(NaphM₄L₂)₂** show a significant splitting of the oxidation wave, providing evidence of electronic interactions between DTF units. A similar splitting was already reported in the case of TTF-based molecular tweezers and was ascribed to the formation of mixed valence and π -dimer species.^[9e] From a mechanistic point of view the electrochemical process observed for the **(NaphM₄L₂)₂** dimer consists of two successive oxidations, each involving two electrons (Figure 7a). Cyclic voltammetry was also considered in order to monitor the recognition process of DCTNF by **(NaphM₄L₂)₂** (Figure 6b). Addition of increasing amount of DCTNF leads to a shift of the binding equilibrium toward the host-guest complex formation, resulting in the disappearance of the oxidation process splitting according to the square scheme shown in Figure 7b. The DCTNF \subset **NaphM₄L₂** host-guest complex exhibits a unique oxidation process at $E_{1^{ox}} = 0.58$ V vs Fc/Fc⁺ (Figure 6b). Interestingly, two reduction waves remain during the reduction scan, which occur at potentials very similar to those of the dimeric **(NaphM₄L₂)₂** self-assembly (Figure 6a). The reduction event may therefore be ascribed to the **(NaphM₄L₂)₂**⁴⁺ species that is recovered while releasing the encapsulated DCTNF (Figures 1 and 7). One will note that the release process is reversible since the voltammogram remains identical after several cycles (Figure S19). In order to get a deeper understanding of the release/uptake mechanism, theoretical voltammograms were simulated both in absence and presence of the guest, taking into account equilibria

illustrated in Figure 7c. Those electrochemical simulations fit nicely with the experimental CVs (Figure 6c) and confirm that this redox-triggered release process is driven by the highly favorable dimerization process of oxidized **NaphM₄L₂**²⁺ tweezers (see SI).

In summary, two novel self-assembled metalla-tweezers were designed from an electron-rich DTF-based ligand and hydroxyquinonato diruthenium complexes. The larger **NaphM₄L₂** tweezer shows a distance of ca 7 Å between both redox-active tips. Such geometry proves to be favourable for a spontaneous dimerization **((NaphM₄L₂)₂)**, which could be characterized in solution, in the gas phase and in the solid state. Remarkably, this interpenetrated arrangement can be dissociated in presence of an electron-poor DCTNF unit, leading to a 1:1 host-guest complex (DCTNF \subset **NaphM₄L₂**) as shown by NMR and HRMS-FTICR experiments. Finally, electrochemical oxidation of the latter host-guest complex allows for regenerating the dimeric structure thanks to favourable interactions between the oxidized tweezer-like molecules, resulting in a concomitant original redox-controlled delivering of the DCTNF guest molecule. Work is underway to extend this new efficient approach in guest delivering, to new redox-active molecular tweezers.

Acknowledgements

The authors gratefully acknowledge the French Embassy in Kiev (Ukr) for PhD grants (SK and MD). They also acknowledge the ASTRAL platform (SFR MATRIX, Univ. Angers) for their assistance in spectroscopic analyses.

Keywords: Host-guest systems • Molecular tweezers • Self-assembly • Sulfur-heterocycles • Supramolecular chemistry

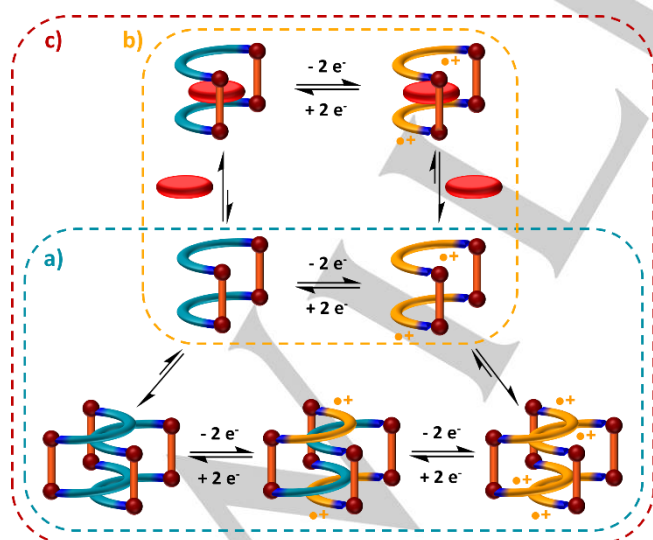


Figure 7. Scheme illustrating equilibria occurring during a) the redox process involving the **(NaphM₄L₂)₂** dimer, b) the redox-triggered guest release process involving the **NaphM₄L₂** monomer and c) the complete redox mechanism involved in the guest release process.

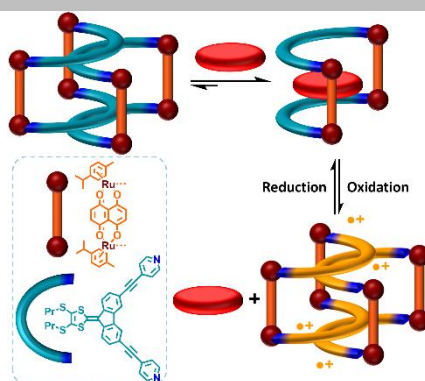
- [1] a) B. Li, T. He, Y. Fan, X. Yuan, H. Qiu, S. Yin, *Chem. Commun.* **2019**, 55, 8036-8059; b) T. R. Cook, P. J. Stang, *Chem. Rev.* **2015**, 115, 7001-7045.
- [2] A. Casini, B. Woods, M. Wenzel, *Inorg. Chem.* **2017**, 56, 14715-14729.
- [3] a) S. Zarra, D. M. Wood, D. A. Roberts, J. R. Nitschke, *Chem. Soc. Rev.* **2015**, 44, 419-432; b) H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, 112, 2015-2041.
- [4] T. Y. Kim, R. A. S. Vasdev, D. Preston, J. D. Crowley, *Chem. Eur. J.* **2018**, 24, 14878-14890.
- [5] V. Croué, S. Goeb, M. Sallé, *Chem. Commun.* **2015**, 51, 7275-7289.
- [6] a) S. Bivaud, S. Goeb, V. Croué, P. I. Dron, M. Allain, M. Sallé, *J. Am. Chem. Soc.* **2013**, 135, 10018-10021; b) S. Bivaud, J. Y. Balandier, M. Chas, M. Allain, S. Goeb, M. Sallé, *J. Am. Chem. Soc.* **2012**, 134, 11968-11970; c) S. Goeb, S. Bivaud, P. I. Dron, J.-Y. Balandier, M. Chas, M. Sallé, *Chem. Commun.* **2012**, 48, 3106-3108.
- [7] a) G. Szalóki, V. Croué, V. Carré, F. Aubriet, O. Alévêque, E. Levillain, M. Allain, J. Arago, E. Orti, S. Goeb, M. Sallé, *Angew. Chem. Int. Ed.* **2017**, 56, 16272-16276; b) V. Croué, S. Goeb, G. Szalóki, M. Allain, M. Sallé, *Angew. Chem. Int. Ed.* **2016**, 55, 1746-1750.
- [8] a) M. Hardouin-Lerouge, P. Hudhomme, M. Sallé, *Chem. Soc. Rev.* **2011**, 40, 30-43; b) J. Leblond, A. Petitjean, *Chemphyschem* **2011**, 12, 1043-1051.
- [9] a) S. Bähring, H. D. Root, J. L. Sessler, J. O. Jeppesen, *Org. Biomol. Chem.* **2019**, 17, 2594-2613; b) A. Jana, S. Bähring, M. Ishida, S. Goeb, D. Canvet, M. Sallé, J. O. Jeppesen, J. L. Sessler, *Chem. Soc. Rev.* **2018**, 47, 5614-5645; c) J. S. Park, J. L. Sessler, *Acc. Chem. Res.* **2018**, 51, 2400-2410; d) A. Jana, M. Ishida, J. S. Park, S. Bähring, J. O. Jeppesen, J. L. Sessler, *Chem.*

- Rev. **2017**, *117*, 2641-2710; e) Y. Cotellet, M. Hardouin-Lerouge, S. Legoupy, O. Alévêque, E. Levillain, P. Hudhomme, *Beilstein J. Org. Chem.* **2015**, *11*, 1023-1036; f) M. Hardouin-Lerouge, Y. Cotellet, S. Legoupy, P. Hudhomme, *New J. Chem.* **2014**, *38*, 5341-5348; g) M. H. Düker, H. Schäfer, M. Zeller, V. A. Azov, *J. Org. Chem.* **2013**, *78*, 4905-4912; h) T. Poulsen, K. A. Nielsen, A. D. Bond, J. O. Jeppesen, *Org. Lett.* **2007**, *9*, 5485-5488; i) K. A. Nielsen, W.-S. Cho, J. O. Jeppesen, V. M. Lynch, J. Becher, J. L. Sessler, *J. Am. Chem. Soc.* **2004**, *126*, 16296-16297.
- [10] a) Y. Lu, H.-N. Zhang, G.-X. Jin, *Acc. Chem. Res.* **2018**, *51*, 2148-2158; b) W. M. Bloch, G. H. Clever, *Chem. Commun.* **2017**, *53*, 8506-8516; c) S.-L. Huang, T. S. A. Hor, G.-X. Jin, *Coord. Chem. Rev.* **2017**, *333*, 1-26; d) L. Xu, Y. X. Wang, L. J. Chen, H. B. Yang, *Chem. Soc. Rev.* **2015**, *44*, 2148-2167; e) J. J. Henkelis, M. J. Hardie, *Chem. Commun.* **2015**, *51*, 11929-11943; f) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848-1860; g) A. Mishra, S. C. Kang, K.-W. Chi, *Eur. J. Inorg. Chem.* **2013**, 5222-5232; h) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810-6918.
- [11] S. Krykun, M. Allain, V. Carré, F. Aubriet, Z. Voitenko, S. Goeb, M. Sallé, *Inorganics* **2018**, *6*, 44.
- [12] H. Yan, G. Süss-Fink, A. Neels, H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.* **1997**, 4345-4350.
- [13] a) L. Avram, Y. Cohen, *Chem. Soc. Rev.* **2015**, *44*, 586-602; b) A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, *Chem. Soc. Rev.* **2008**, *37*, 479-489.
- [14] N. P. E. Barry, J. Furrer, B. Therrien, *Helv. Chim. Acta* **2010**, *93*, 1313-1328.
- [15] Y. H. Song, N. Singh, J. Jung, H. Kim, E. H. Kim, H. K. Cheong, Y. Kim, K. W. Chi, *Angew. Chem. Int. Ed.* **2016**, *55*, 2007-2011.
- [16] L. Faour, C. Adam, C. Gautier, S. Goeb, M. Allain, E. Levillain, D. Canevet, M. Sallé, *Chem. Commun.* **2019**, *55*, 5743-5746.
- [17] F. Aparicio, L. Faour, M. Allain, D. Canevet, M. Sallé, *Chem. Commun.* **2017**, *53*, 12028-12031.
- [18] a) D. F. Perepichka, I. F. Perepichka, O. Ivasenko, A. J. Moore, M. R. Bryce, L. G. Kuz'mina, A. S. Batsanov, N. I. Sokolov, *Chem. Eur. J.* **2008**, *14*, 2757-2770; b) S. Amriou, C. Wang, A. S. Batsanov, M. R. Bryce, D. F. Perepichka, E. Ortí, R. Viruela, J. Vidal-Gancedo, C. Rovira, *Chem. Eur. J.* **2006**, *12*, 3389-3400.

Entry for the Table of Contents

COMMUNICATION

A redox-active coordination tweezer constructed from the dithiol-fluorene (DTF) framework spontaneously dimerizes in solution thanks to favourable geometric and electronic parameters. The interconnected dimer can be dissociated upon forming a 1:1 host-guest complex in presence of an electron-poor guest. The latter can be reversibly released upon oxidation, through an original exchange process.



Serhii Kryhun, Maksym Dekhtiarenko, David Canevet Vincent Carré, Frédéric Aubriet, Eric Levillain, Magali Allain, Zoia Voitenko, Marc Sallé* and Sébastien Goeb*

Page No. – Page No.

**Metalla-Assembled Electron-Rich
Tweezers: Original Redox-
Controlled Guest Release through
Supramolecular Dimerization**