Electronic Supplementary Information

Synthesis, Characterization, Optical Absorption/Fluorescence Spectroscopy, and Second-Order Nonlinear Optical Properties of Aggregate Molecular Architectures of Unsymmetrical Schiff-Base Zinc(II) Complexes

Ivan Pietro Oliveri,[a] Salvatore Failla,[b] Alessia Colombo,[c] Claudia Dragonetti,[c,d] Stefania Righetto[c] and Santo Di Bella*[a]

Contents

I. Additional ^{1}H NMR Spectra ..…….. S2
II. Additional Optical Absorption and Fluorescence Spectra …….. S5
III. DOSY NMR Data and Estimation of the Molecular Mass …..…… S8
IV. References ..…….. S9

[a]*Dipartimento di Scienze Chimiche, Università di Catania, I-95125 Catania, Italy. E-mail: sdibella@unict.it; Fax: +39 095 580138; Tel: +39 095 738 5068*

[b]*Dipartimento di Ingegneria Industriale, Università di Catania, I-95125 Catania, Italy*

[c]*Dipartimento di Chimica dell'Università degli Studi di Milano, UdR di Milano dell'INSTM, and*

[d]*Istituto di Scienze e Tecnologie Molecolari del CNR, I-20133 Milano, Italy*

I. Additional ^{1}H NMR Spectra

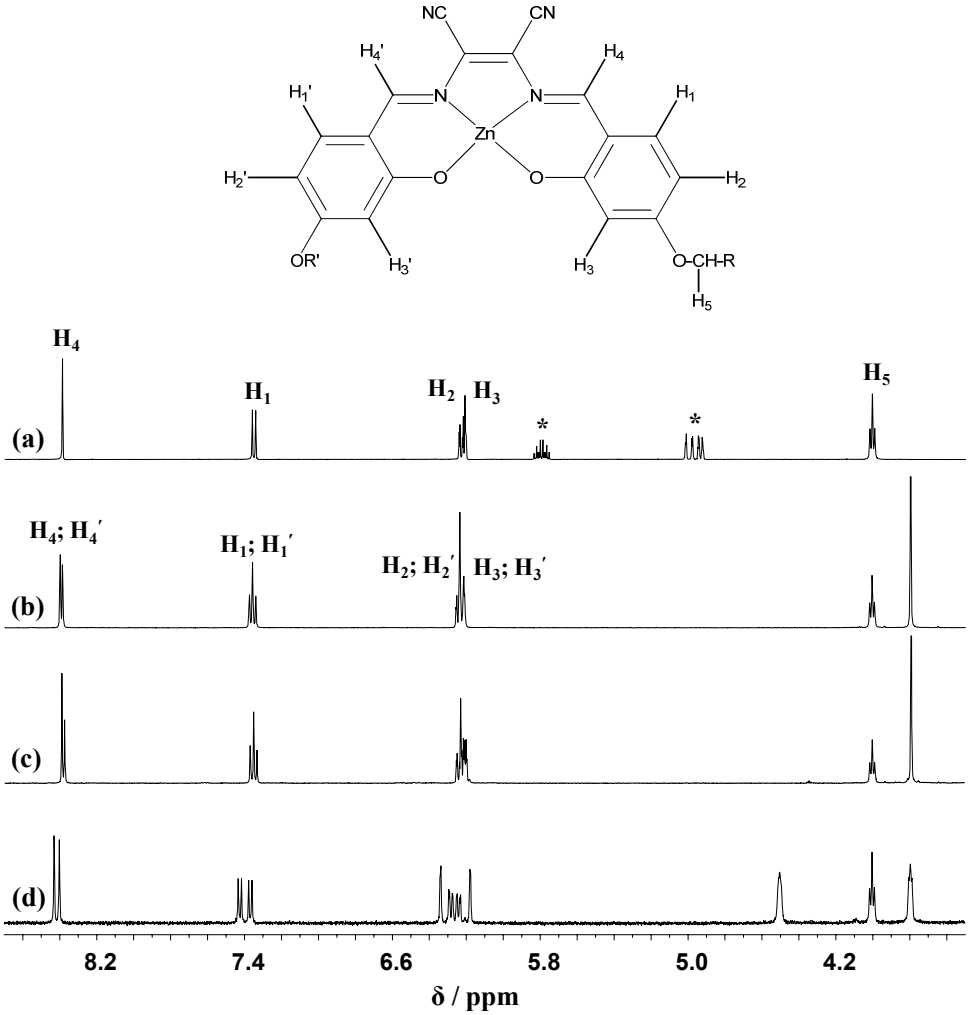

Fig. S1. ^{1}H NMR spectra of **1 (b)**, **2 (c)** and **3 (d)** in DMSO-d_6. The ^{1}H NMR spectrum of **4** in DMSO-d_6 is reported for comparison **(a)**. The asterisked peaks refer to -C*H*=CH_2 signals of the 4-(undec-10-enyloxy) chains.

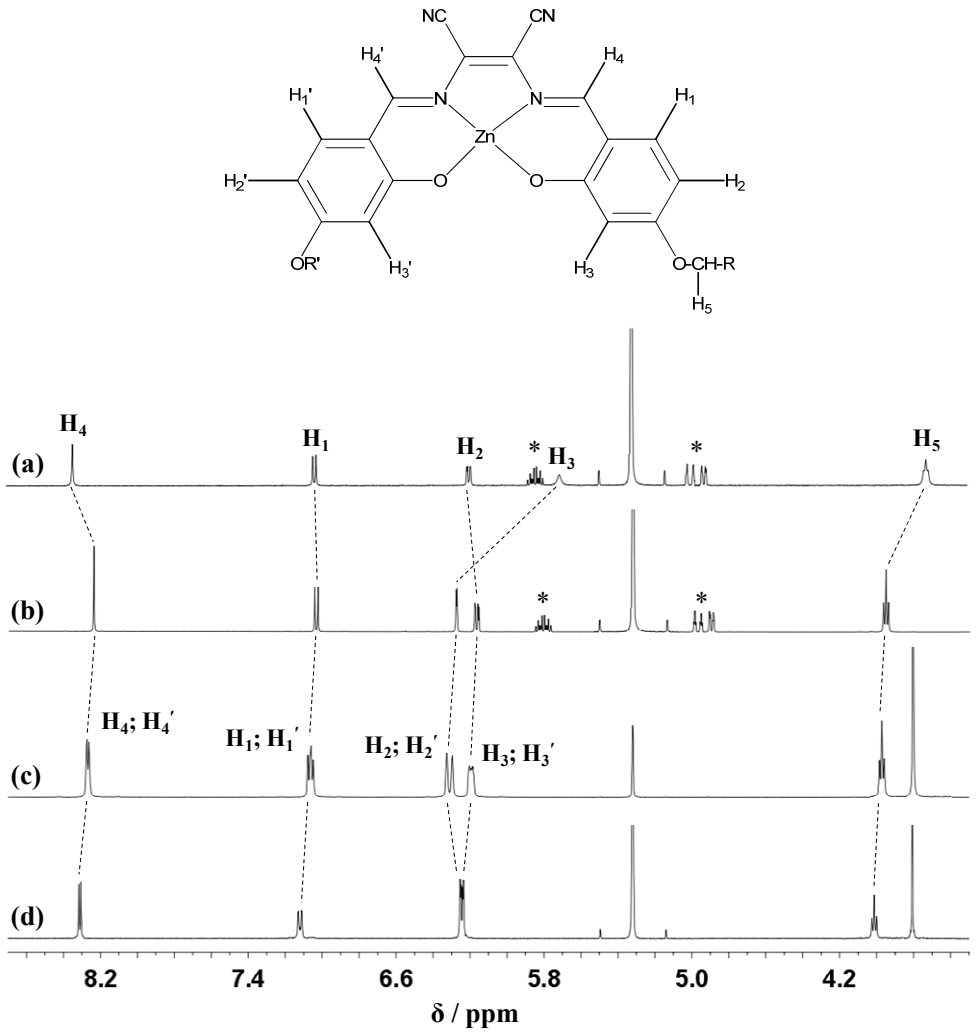

Fig. S2. Comparison of ^{1}H NMR spectra of **4 (a)**, **4**·BrTBA **(b)**, **1**·BrTBA **(c)** and **2 (d)** in DCM-d_2. The asterisked peaks refer to -C*H*=CH_2 signals of the 4-(undec-10-enyloxy) chains of **4**. The addition of BrTBA to a DCM-d_2 solution of **4** results in a sizable down-field shift of H_3 and H_5 signals, in agreement with the deaggregation process and formation of the **4**·BrTBA adduct.[1]

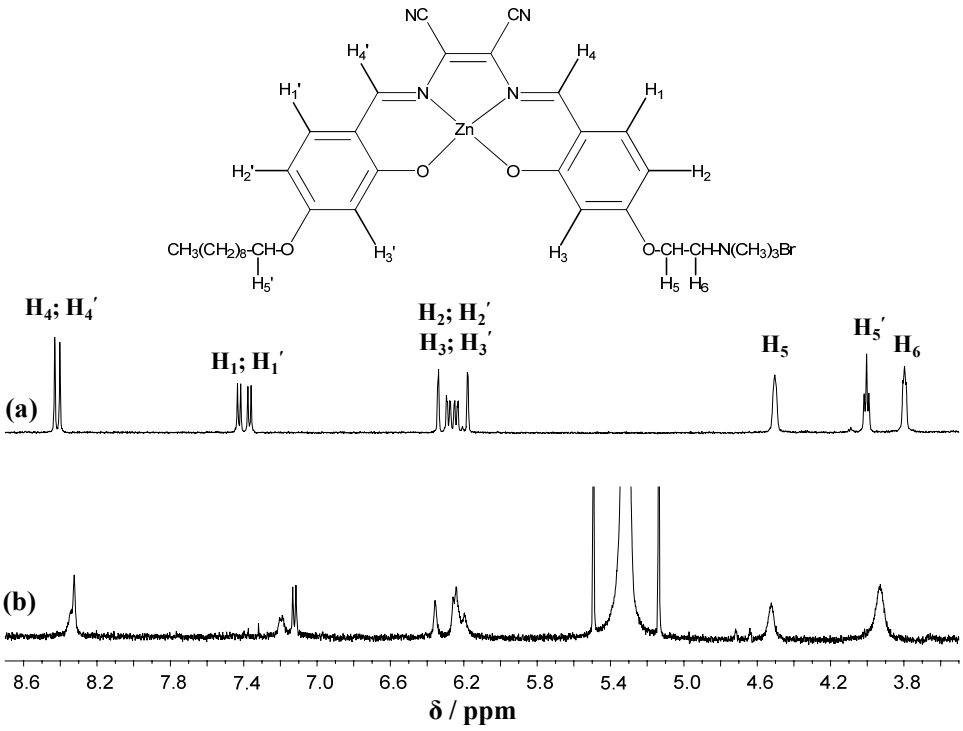

Fig. S3. ^{1}H NMR spectra of **3** in DMSO-d_6 **(a)** and DCM-d_2 **(b)**.

II. Additional Optical Absorption and Fluorescence Spectra

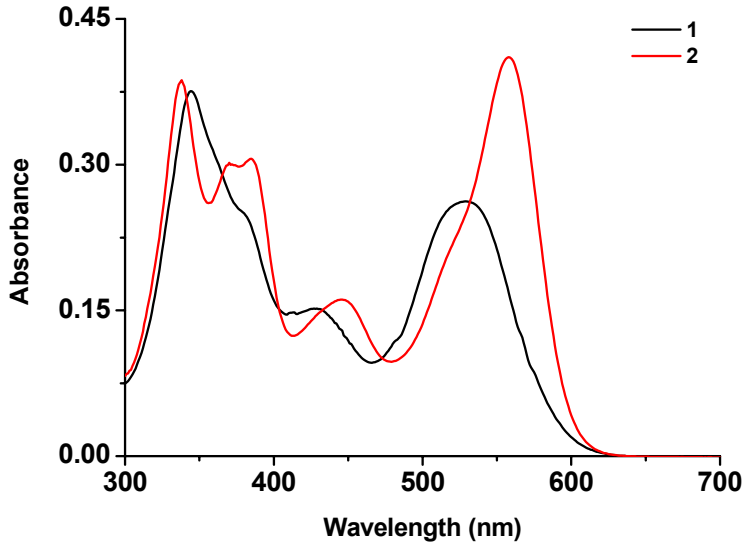

Fig. S4. UV/vis absorption spectra of **1** (−) and **2** (−) (1.0×10^{-5} M solutions) in DCM.

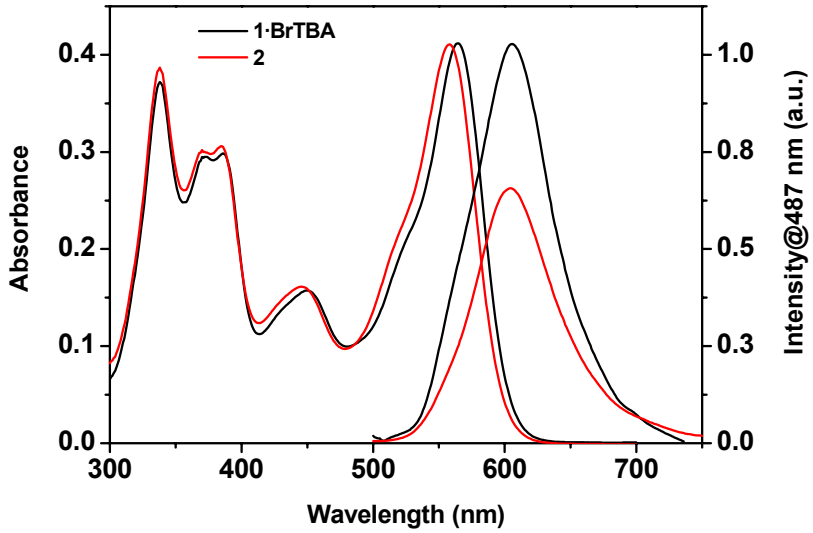

Fig. S5. UV/vis absorption and fluorescence (λ_{exc} = 487 nm) spectra of **1**·BrTBA (−) and **2** (−) (1.0 × 10^{-5} M solutions) in DCM.

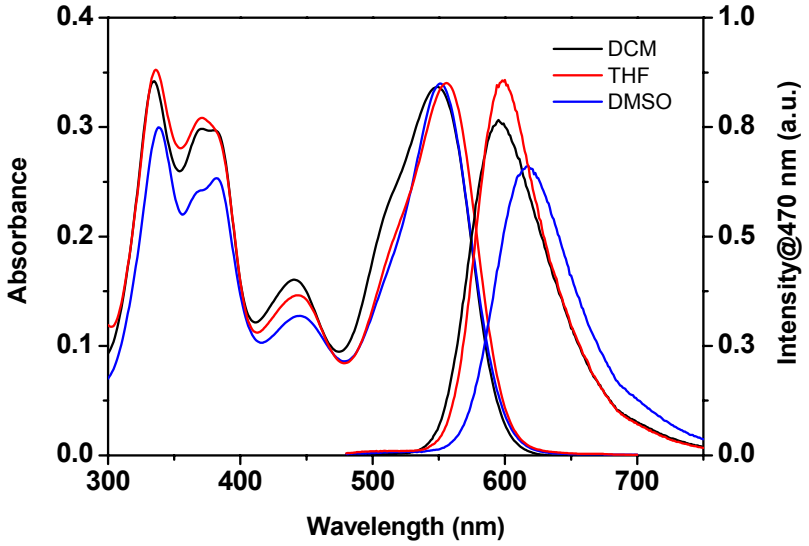

Fig. S6. UV/vis absorption and fluorescence (λ_{exc} = 470 nm) spectra of **3** (1.0 × 10^{-5} M) in DCM (−), THF (−) and DMSO (−).

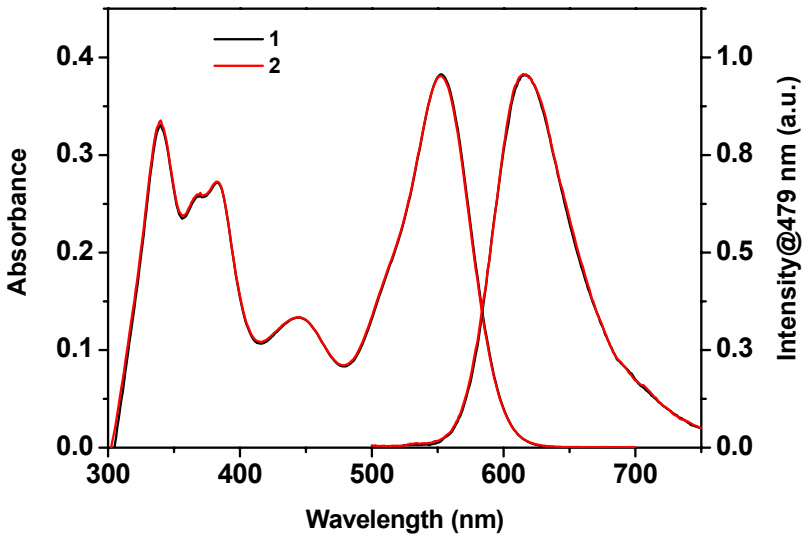

Fig. S7. UV/vis absorption and fluorescence (λ_{exc} = 479 nm) spectra of **1** and **2** (1.0×10^{-5} M solutions) in DMSO.

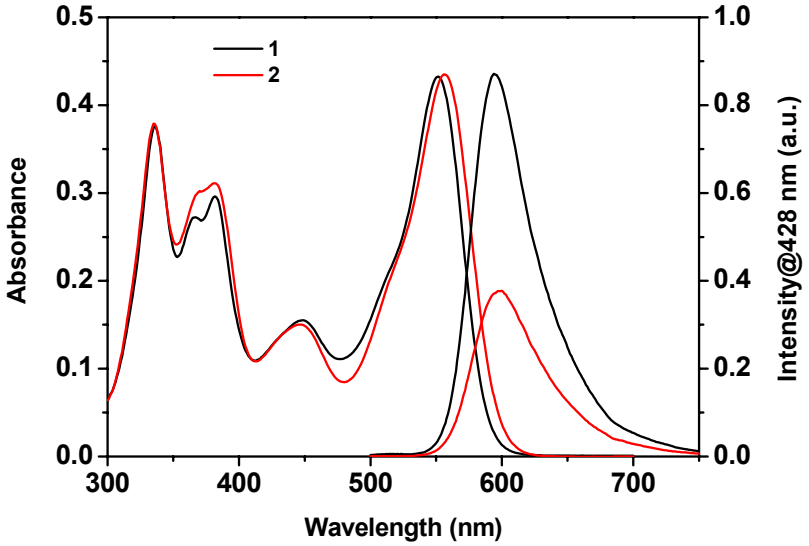

Fig. S8. UV/vis absorption and fluorescence (λ_{exc} = 428 nm) spectra of **1** and **2** (1.0×10^{-5} M solutions) in THF.

III. DOSY NMR Data and Estimation of the Molecular Mass

We have used DOSY as independent method to estimate the molecular mass of the species present in solution.[2] However, the non-spherical nature of the involved molecules does not allow any straightforward application of the Stokes-Einstein equation, as normally used to estimate the molecular size through the measurement of the diffusion coefficient, D.[3] Thus, to achieve reliable molecular masses from DOSY measurements, we have chosen to estimate them by using a known internal reference species thus obtaining the molecular mass by their relative diffusion coefficient.[4,5]

The molecular mass in solution, m, was simply estimated using Graham's law of diffusion: $D = K(T / m)^{1/2}$, where the constant K depends on geometric factors, including the area over which the diffusion is occurring. By assuming a constant temperature and that K is the same for both species in solution, the relative diffusion rate of two species A and B is given by: $D_A/D_B = (m_B/m_A)^{1/2}$. This allows the calculation of an unknown molecular mass by eq. 1:

$$m_B = m_A (D_A/D_B)^2 \qquad \text{(S1)}$$

Therefore, the diffusion rate values obtained by DOSY can be used to estimate the molecular mass of a species, by comparison with the actual D value of a known internal reference (*e.g.*, the solvent).[4b,5]

A representative 2D DOSY plot of **2** is shown in Fig. S9. It is important to note that peaks from molecules with different diffusion rates appear in different positions on the y-axis (diffusion rate) and can easily be assigned to each molecule. Using the cursor in VNMRJ, in the case of **2** in DCM-d_2 maxima were found corresponding to $D = 36.00 \times 10^{-10}$ m^2 s^{-1}, for the solvent,[6] and $D = 9 \times 10^{-10}$ m^2 s^{-1}, for the complex (Fig. S9). The ^{1}H signal in DCM-d_2 is related to CCl_2HD, with a molecular mass of 85.941 Da. Therefore, using these data and applying eq. S1 a mass of 1375.06 Da is calculated, in agreement with the presence of a dimeric species (1464.12 Da) in solution.

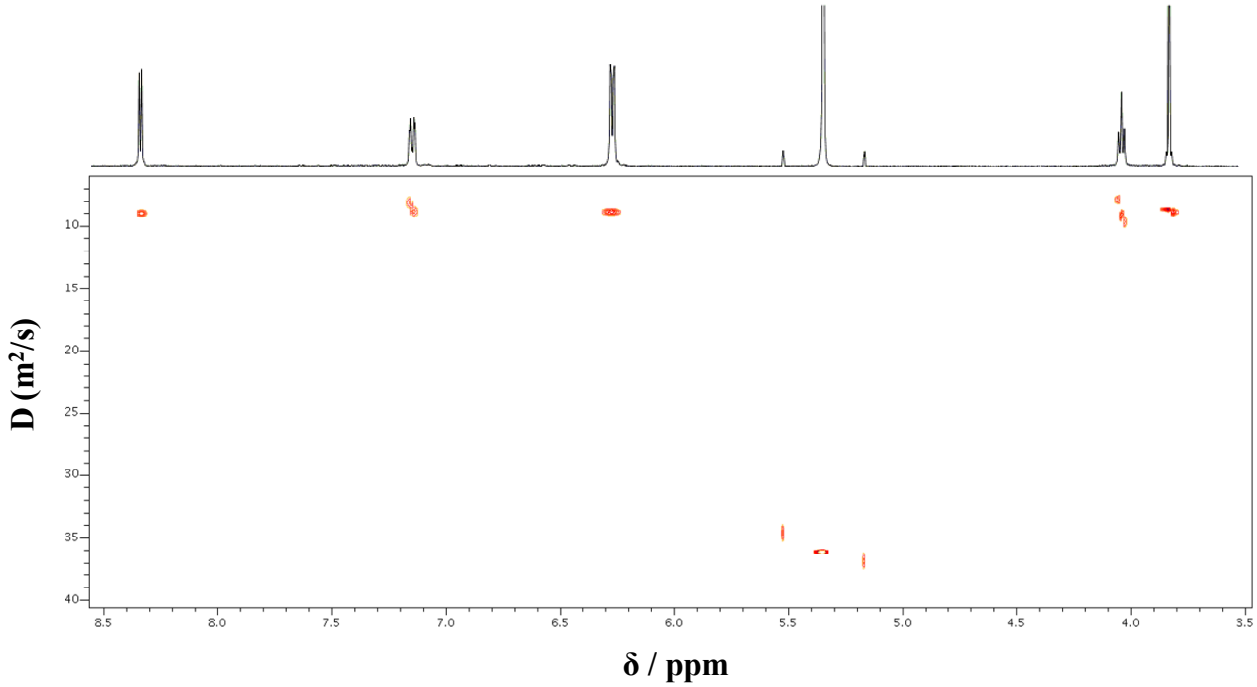

Fig. 9. ^{1}H NMR DOSY spectrum of **2** in DCM-d_2.

References

1. I. P. Oliveri, S. Failla, G. Malandrino and S. Di Bella, *New J. Chem.*, 2011, **35**, 2826.
2. *(a)* C. S. Johnson Jr., *Prog. Nucl. Magn. Reson.*, 1999, **34**, 203; *(b)* K. F. Morris and C. S. Johnson Jr., *J. Am. Chem. Soc.*, 1992, **114**, 3139.
3. *(a)* A. Macchioni, G. Ciancaleoni, C. Zuccaccia and D. Zuccaccia, *Chem. Soc. Rev.*, 2008, **37**, 479; *(b)* P. S. Pregosin, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2006, **49**, 261; *(c)* F. Song, S. J. Lancaster, R. D. Cannon, M. Schormann, S. M. Humphrey, C. Zuccaccia, A. Macchioni and M. Bochmann, *Organometallics*, 2005, **24**, 1315.
4. See, for example: (a) G. Kagan, W. Li, R. Hopson and P. G. Williard, *J. Am. Chem. Soc.*, 2011, **133**, 6596; J. Fielden, D. Long, A. M. Z. Slawin, P. Ko1gerler and L. Cronin, *Inorg. Chem.*, 2007, **46**, 9090.
5. (*a*) G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri and S. Di Bella, *Inorg. Chem.*, 2012, **51**, 8409; (*b*) G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri and S. Di Bella, *Dalton Trans.*, 2012, **41**, 387; (*c*) G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri, R. Purrello and S. Di Bella, *Inorg. Chem.*, 2010, **49**, 5134.
6. D. Li, G. Kagan, R. Hopson and P. G. Williard, *J. Am. Chem. Soc.*, 2009, **131**, 5627.