

Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Ultrafast static and diffusion-controlled electron transfer at Ag₂₉ nanocluster/molecular acceptor interfaces

Cite this: DOI: 10.1039/x0xx00000x

Shawkat M. Aly,^{a,‡} Lina G. AbdulHalim,[‡] Tabot M.D. Besong, Giada S. Soldan, Osman M. Bakr,^{*} and Omar F. Mohammed^{*}

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

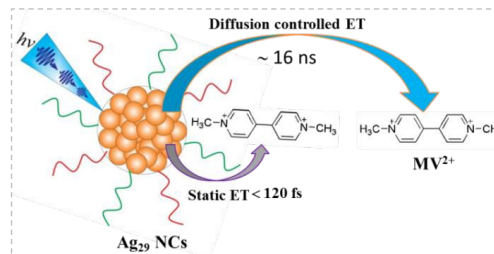
www.rsc.org/

Abstract: The efficient absorption of visible light and a long-lived excited state lifetime of silver nanoclusters (Ag₂₉ NCs) are integral properties for these new clusters to serve as light-harvesting materials. Upon optical excitation, electron injection at Ag₂₉ NC/methyl viologen (MV²⁺) interfaces is very efficient and ultrafast. Interestingly, our femto- and nanosecond time-resolved results demonstrate clearly that both dynamic and static electron transfer mechanisms are involved in photoluminescence quenching of Ag₂₉ NC.

The pursuit of new light-absorbing candidates for solar cell applications is a topic that has garnered intensive efforts by materials scientists. A relatively new class of nanomaterials called metal nanoclusters (NCs) has emerged as the missing link between atomic and nanoparticle behavior in metals.^{1, 2} These are atomically precise nanoparticles, less than 2 nm in size, which consist of a distinct number of metal atoms protected by organic ligands.³ In this size regime, metals behave like molecules, whereby their energy levels discretize and increase in spacing.⁴⁻⁷ NCs are well documented for their wide applications as fluorescent probes for ion detection,^{8, 9} biosensing^{10, 11} and gas sensing,¹² and specifically for the ultrafast electron transfer (ET) in pyrene-functionalized gold (Au₂₅) NCs.¹³ Furthermore, Au NCs have recently been reported as photosensitizers in mesoscopic TiO₂-based solar cells.¹⁴ This specific example highlighted the importance of the photoactivity of thiolated metal clusters for high-power conversion efficiency. While Ag NCs have been explored for their ET and sensitization potential, they have received far less attention than Au NCs, despite their obvious advantages: low cost, strong photoluminescence (PL), demonstrable stability, and uniquely ultra-scalable synthesis in high-yield and molecular purity.¹⁵⁻¹⁷ PL in metal NCs is thought to originate from either the metal core¹⁸ or from interactions between

the metal core and surface ligand.^{2, 19, 20} To date, only a few examples of Ag NCs with a short lifetime have proven to show photoinduced-electron-transfer (PET) properties.²¹⁻²⁴ However, little progress has been made towards uncovering PET reaction mechanisms in the nanocluster community; more efforts are needed to better understand the excited-state interaction and the subsequent development of applications for NCs, especially in energy conversions. As part of the regime, methyl viologen (MV²⁺), an organic dication, is a highly attractive choice for investigating donor-acceptor properties because of its strong electron accepting character and wide range of applications including solar energy conversion.²⁵⁻²⁷ The stability of its radical cation (MV^{+•}) and the ease of its spectroscopic detection makes MV²⁺ a favorable choice in applications explaining the fundamentals of PET.^{25, 28, 29}

In this work, we investigate the excited-state interaction between Ag₂₉ NCs and MV²⁺ using steady-state and state-of-the-art femtosecond laser spectroscopy with broadband capabilities. Our results indicate an efficient quenching of Ag NC fluorescence in the presence of MV²⁺. Synthesis and characterization of the Ag₂₉ NCs is detailed in the supporting information. In addition, single crystal of these clusters has been recently reported.³⁰ Stern-Volmer plots confirmed a combination of dynamic and static mechanisms (see Scheme 1). This mixed interaction mechanism was further supported by time-resolved femto- and nanosecond transient absorption (fs-TA and ns-TA) and time-correlated single photon counting (TCSPC) measurements. Additionally, the ultrafast ET from the NCs into MV²⁺ was indicated by the formation of the MV^{+•} within 120 fs.



Scheme 1. Static and diffusion-controlled mechanisms of PET from Ag₂₉ NC to MV²⁺.

Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia.

*Email: osman.bakr@kaust.edu.sa; omar.abdelsaboer@kaust.edu.sa

Electronic Supplementary Information (ESI) available. See ODI:

[‡] The authors contributed equally to this work. ^aOn leave from the chemistry department, Assiut University, Egypt.

Figure 1 presents the steady-state absorption and emission spectra of Ag_{29} NC with and without MV^{2+} in deaerated acetonitrile (CH_3CN). In the absence of MV^{2+} , the absorption spectrum of NCs shows three absorption bands at 320, 445 and 510 nm. However, upon MV^{2+} addition, the spectrum features a slight increase in absorption and a long tail over the range of 500–700 nm, providing clear evidence for the ground-state interaction between the two components.

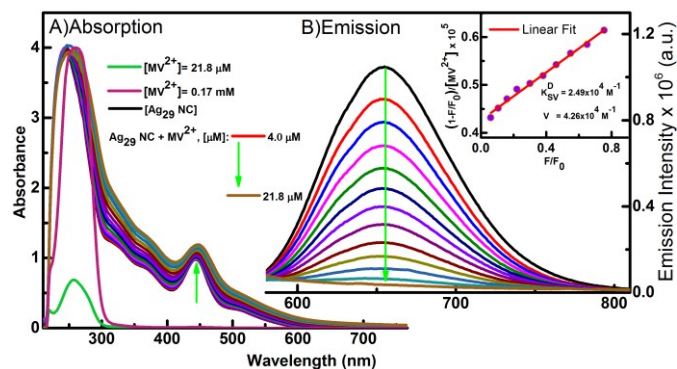


Figure 1. Steady-state absorption (A) and emission (B) spectra of a deaerated CH_3CN solution of Ag_{29} NCs (3 mg/mL) in the presence and absence of MV^{2+} . Inset is a Stern-Volmer plot with the static (V) and dynamic (K_{SV}^D) quenching rate constant as obtained from straight line.

Photoexcitation of the Ag_{29} NC shows an intense emission spectrum centered at 660 nm, while efficient quenching became evident upon the addition of MV^{2+} ; a maximum quenching of $\sim 99\%$ is observed with $\sim 21.8 \mu\text{M}$ - MV^{2+} added. The absorption spectra of two different concentrations of $\text{MV}^{2+} = 4$ and $21.8 \mu\text{M}$ is given in Figure 1 for comparison. The lower concentration is equal to the highest concentration used to induce maximum quenching during NC luminescence and the other is about 8-folds higher; however, neither showed any spectral overlap with Ag_{29} NC emission, ruling out a photo-induced energy transfer process from NCs to MV^{2+} . Moreover, association of the cluster can also be ruled out based on the control experiment performed using three different concentrations of NCs, where quenching behavior in the presence of MV^{2+} proven to be the same, see Figure S8. Therefore, we can confidently assign this strong quenching to a PET from Ag_{29} NC to MV^{2+} , which is indicative of a strong excited-state interaction. Several reports have evidenced fluorescence quenching of Ag NCs upon interaction with electron acceptors.^{22, 23, 31} Here, we analyzed PL quenching data using the Stern-Volmer equation, $(F_0/F) = 1 + K_{SV}[MV^{2+}]$, where F_0 and F are the fluorescence intensities before and after the addition of MV^{2+} , respectively; K_{SV} is the quenching constant; and $[MV^{2+}]$ is the concentration of MV^{2+} . The upward curve observed on the Stern-Volmer plots indicates a combined affect from both diffusion-controlled and static mechanisms in the excited-state deactivation.³² Quenching data were further analyzed using an extended Stern-Volmer equation: $\frac{(1-F/F_0)}{[MV^{2+}]} = K_{SV}^D \left(\frac{F}{F_0}\right) + V$, where both static (V) and dynamic (K_{SV}^D) quenching constants are considered.^{33, 34} The data show a straight line with a correlation coefficient of 0.99 with estimated dynamic and static quenching constants of $2.49 \times 10^4 \text{ M}^{-1}$ and $4.26 \times 10^4 \text{ M}^{-1}$, respectively. Time-resolved spectroscopy further confirmed a mixed mechanism of luminescence quenching behavior (see below).

Time-resolved TA spectroscopy has proven to be a critical part of studying excited-state interactions,³⁵⁻⁴⁰ specifically for probing energy and electron transfer processes in NCs.^{13, 21, 41} Here, we explore the lifetime and light-harvesting capability of Ag_{29} NC using fs- and ns-TA spectroscopy in CH_3CN in the presence and absence of MV^{2+} ; the TA spectra are given in Figures 2 and 3. The experimental setup for TA measurement is described in SI and further details can be found elsewhere.⁴²

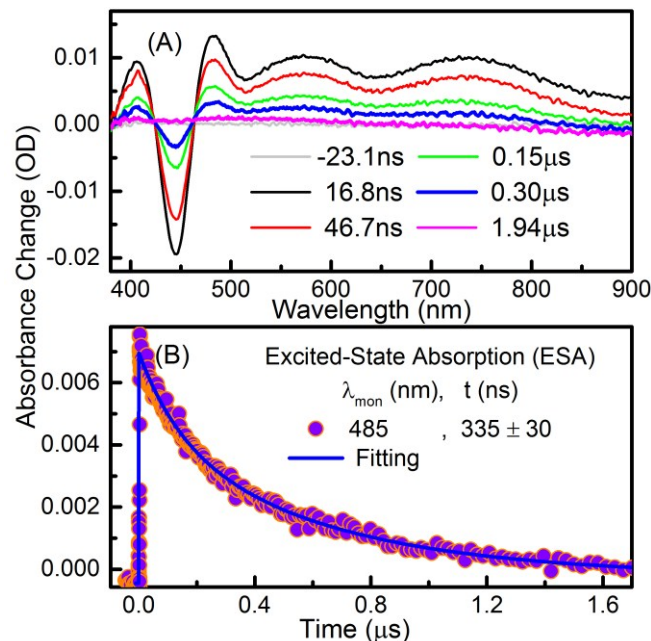


Figure 2. ns-TA of Ag_{29} NCs in deaerated CH_3CN after laser excitation at 350 nm (A) and kinetic traces of ESA monitored at 485 nm (B).

ns-TA spectra (Figure 2A) show the excited-state absorption (ESA) maximum at 405 nm. We observed another band with several features extending over the range of 485–850 nm together with the ground-state bleach (GSB) at 445 nm. Figure 2B shows the ESA decay, monitored at 485 nm, where the extracted lifetime of Ag_{29} NC is estimated to be 335 ± 30 ns. In contrast, data from previous works for smaller NCs reported much shorter lifetimes than what we report here.^{21, 41} Our extended excited-state lifetime suggests that these NCs may be suitable for use as a photosensitizer. To extend our understanding of the excited-state interaction between Ag_{29} NC and MV^{2+} , we performed fs-TA in the presence and absence of two different concentrations of MV^{2+} , after laser excitation at 350 nm (see Figure 3).

TA spectra of Ag_{29} NC alone showed less than a 10% decrease in ESA and GSB recovery over a time frame of 5.5 ns, which agrees with the long lifetime extracted from the ns-TA decay. Dynamics of the excited state show a faster decay with added MV^{2+} that speeds up with increasing concentration. Moreover, a new spectral band developed and became more feasible at higher concentrations of MV^{2+} and with the increased delay time at 605 nm. This new band lies within the spectral range reported in the literature for radical $\text{MV}^{\bullet+}$.^{25, 43} The formation of the $\text{MV}^{\bullet+}$ provides clear evidence for the PET from NC to MV^{2+} . Figures 4A and B illustrate the kinetic traces of NCs with and without MV^{2+} .

In the presence of MV^{2+} , the radical ion forms ultrafast within 120 fs (the temporal resolution of our instrument, see Figure S1 for pulse characterization), followed by decay due to a charge recombination (CR) with a time constant of 41 ± 5 ps, evidenced by ESA and GSB behavior. This rapid dynamic provides more experimental evidence for a close connection between NCs and MV^{2+} , and indicates that PET processes occur between them. More specifically, the formation of radical ions, immediately after pulse excitation, evidences that the electron transfer process from NCs and MV^{2+} is static in nature.

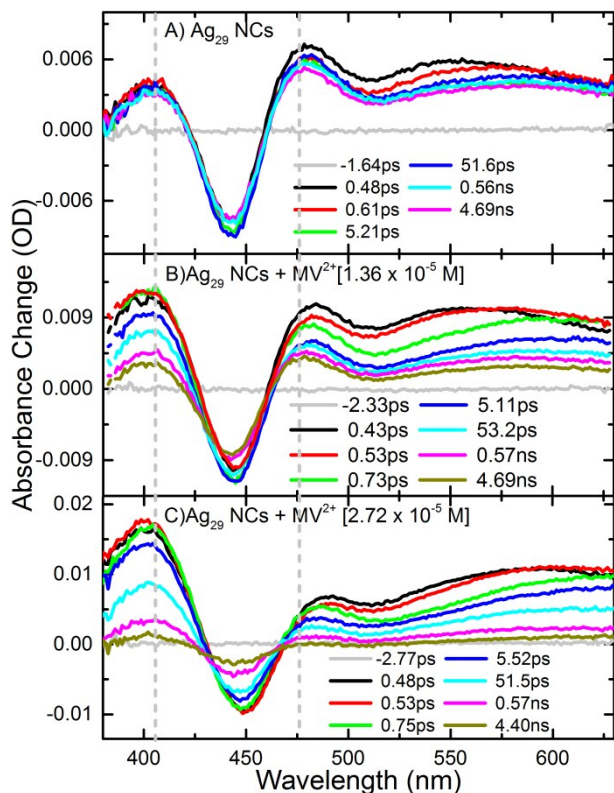


Figure 3. fs-TA of Ag_{29} NCs in deaerated CH_3CN after 350 nm laser excitation: **A)** free, in the presence of MV^{2+} , **B)** 1.36×10^{-5} M, and **C)** 2.72×10^{-5} M; delay time is given on the graph.

However, it is clear from the kinetic trace that while the fast decay component was about 40%, another long component represents ~ 60 % of the decay (see green and yellow curves in Figure 4A), which is longer than the 2.5 ns time window. While the fast component was estimated at ~ 41 ps and assigned to CR as discussed above, the long component can be attributed to diffusion electron transfer and the lifetime of unreacted NCs. To further explain the kinetics at a longer time scale, we measured the excited-state deactivation using both ns-TA and TSCPC for Ag_{29} NCs in the presence and absence of MV^{2+} ; Figures 4B and C show the kinetics traces. The kinetic decays clearly show a decrease in the excited-state lifetime of the cluster in the presence of MV^{2+} . Such a change in the lifetime of the NCs with added MV^{2+} is indicative of the dynamic nature of the interaction that is involved in the electron transfer process. The rate of the PET was estimated from the excited-state deactivation at $\approx 5\text{--}6 \times 10^7$ s $^{-1}$. This rate is lower than the diffusion limit of MV^{2+} ($\approx 10^{10}$ M $^{-1}$ s $^{-1}$), confirming the diffusion nature of the electron transfer.^{44, 45} Figures 4B and C illustrate the existence of a long component in the decay curves at about 67%, demonstrating a lifetime of NCs that does not undergoes electron transfer.

From the measurements discussed above, we found that the formation of a radical cation within 120 fs proves electron transfer with a static nature with a PET rate anticipated at $\geq 8.3 \times 10^{12}$ s $^{-1}$. This rate is about two orders of magnitude faster than what has recently been reported for a closely related nanocluster system.²² The rate for the diffusion controlled mechanism, as calculated from change in lifetimes, is indicated by ns-TA and TCSPC measurements at $\sim 5\text{--}6 \times 10^7$ s $^{-1}$. Based on this information, we have estimated the efficiency of PET to be $\sim 95\%$ in good agreement with the estimated value from steady-state measurements. Here, we present the detailed reaction mechanisms by which both static and freely diffusing MV^{2+} molecules accept electrons from newly synthesized Ag_{29} clusters as a model system such that they can be applied to other nanoclusters and molecular acceptors. More importantly, we quantitatively separate the contributions of static and collision-caused photo-induced electron transfer from that of the clusters to MV^{2+} through both transient absorption (TA) and time-resolved fluorescence (TCSPC experiments). Note that the interaction was also proven to be solid-state active. We performed the fs-TA experiments for a spin-coated film of Ag_{29} NC on glass in the presence and absence of MV^{2+} (see Figure S9). In the presence of MV^{2+} , a fast deactivation of the excited-state and characteristic bands for $MV^{+ \bullet}$ were observed, providing clear evidence for the PET in solid-state as well. These bands were detected right after excitation (within 120 fs), supporting the static nature of the interaction.

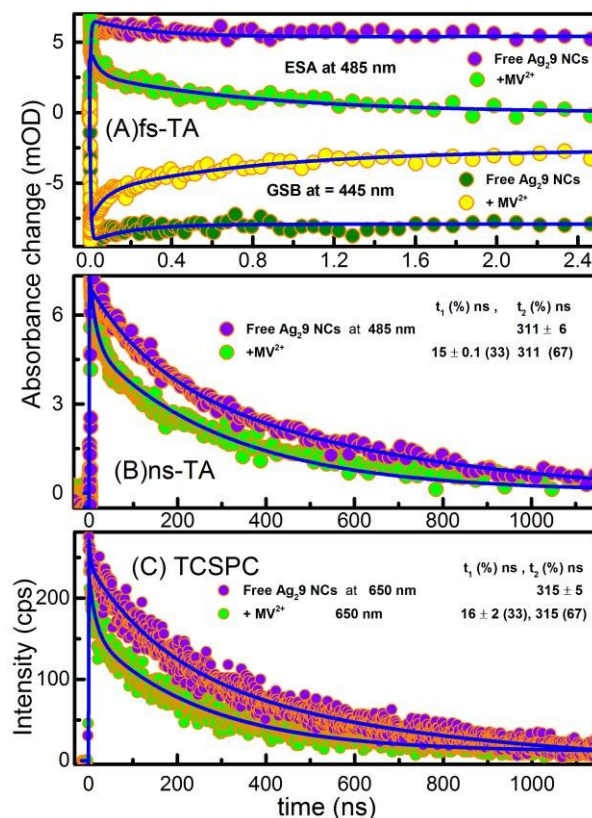


Figure 4. Kinetic traces in deaerated CH_3CN after laser excitation at 350 nm of Ag_{29} NC in the presence (green) and absence (violet) of MV^{2+} collected from **A)** fs-TA monitored at 485 nm (ESA) and 445 nm (GSB), **B)** ns-TA monitored at 485 nm (ESA), and **C)** TCSPC after laser excitation at 485 nm and monitored at $\lambda_{em} = 650$ nm. Fitted lines are given in blue and time constants are given.

Conclusions

Here, we present the light-harvesting capability of Ag₂₉ NCs using both femto- and nanosecond time-resolved laser spectroscopy. We found that these new clusters can serve as an absorber layer in UV-Vis regions with very long excited-state lifetimes. They show rapid and efficient electron injection to the molecular acceptor MV²⁺. Perhaps more importantly, a combination of femto- and nanosecond time-resolved absorption and fluorescence spectroscopies reveals the involvement of two mechanisms by which MV²⁺ induces the decay of the excited state of Ag₂₉ NCs through static and diffusion-controlled electron transfer.

Acknowledgements

The work reported here was supported by King Abdullah University of Science and Technology (KAUST). S.M.A. is grateful for the postdoctoral fellowship provided by Saudi Basic Industries Corporation (SABIC). L. G. A gratefully acknowledges Mr. Alberto Tosato for his assistance with the thin film fabrication.

Notes and references

- 1 L. Shang, S. Dong and G. U. Nienhaus, *Nano Today*, 2011, **6**, 401-418.
- 2 L. Zhang and E. Wang, *Nano Today*, 2014, **9**, 132-157.
- 3 R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. Wang, P. W. Stephens, C. L. Cleveland, W. Luedtke and U. Landman, *Advan. Mater.*, 1996, **8**, 428-433.
- 4 C. M. Aikens, *J. Phys. Chem. A*, 2009, **113**, 10811-10817.
- 5 R. G. Ispasoiu, L. Balogh, O. P. Varnavski, D. A. Tomalia and T. Goodson III, *J. Am. Chem. Soc.*, 2000, **122**, 11005-11006.
- 6 O. Varnavski, G. Ramakrishna, J. Kim, D. Lee and T. Goodson, *J. Am. Chem. Soc.*, 2009, **132**, 16-17.
- 7 Y. Negishi, K. Nobusada and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 5261-5270.
- 8 Z. Chen, D. Lu, G. Zhang, J. Yang, C. Dong and S. Shuang, *Sens. Actuators, B*, 2014, **202**, 631-637.
- 9 Z. Chen, D. Lu, Z. Cai, C. Dong and S. Shuang, *Luminescence*, 2014, **29**, 722-727.
- 10 Q. Cui, Y. Shao, K. Ma, S. Xu, F. Wu and G. Liu, *Analyst*, 2012, **137**, 2362-2366.
- 11 C.-A. J. Lin, T.-Y. Yang, C.-H. Lee, S. H. Huang, R. A. Sperling, M. Zanella, J. K. Li, J.-L. Shen, H.-H. Wang and H.-I. Yeh, *Acs Nano*, 2009, **3**, 395-401.
- 12 G. Korotcenkov, B. K. Cho, L. B. Gulina and V. P. Tolstoy, *Sens. Actuators, B*, 2012, **166-167**, 402-410.
- 13 M. S. Devadas, K. Kwak, J.-W. Park, J.-H. Choi, C.-H. Jun, E. Sinn, G. Ramakrishna and D. Lee, *J. Phys. Chem. Lett.*, 2010, **1**, 1497-1503.
- 14 Y.-S. Chen, H. Choi and P. V. Kamat, *J. Am. Chem. Soc.*, 2013, **135**, 8822-8825.
- 15 T. Udaya Bhaskara Rao and T. Pradeep, *Angew. Chem. Int. Ed.*, 2010, **49**, 3925-3929.
- 16 Z. Wu, E. Lanni, W. Chen, M. E. Bier, D. Ly and R. Jin, *J. Am. Chem. Soc.*, 2009, **131**, 16672-16674.
- 17 L. G. AbdulHalim, S. Ashraf, K. Katsiev, A. R. Kirmani, N. Kothalawala, D. H. Anjum, S. Abbas, A. Amassian, F. Stellacci and A. Dass, *J. Mater. Chem. A*, 2013, **1**, 10148-10154.
- 18 M. S. Devadas, J. Kim, E. Sinn, D. Lee, T. Goodson, III and G. Ramakrishna, *J. Phys. Chem. C*, 2010, **114**, 22417-22423.
- 19 Z. Wu and R. Jin, *Nano letters*, 2010, **10**, 2568-2573.
- 20 T. D. Green and K. L. Knappenberger, *Nanoscale*, 2012, **4**, 4111-4118.
- 21 W.-T. Chen, Y.-J. Hsu and P. V. Kamat, *J. Phys. Chem. Lett.*, 2012, **3**, 2493-2499.
- 22 L. Zhang, J. Zhu, S. Guo, T. Li, J. Li and E. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 2403-2406.
- 23 K. Zhang, K. Wang, X. Zhu, Y. Gao and M. Xie, *Chem. Commun.*, 2014, **50**, 14221-14224.
- 24 S. Jin, S. Wang, Y. Song, M. Zhou, J. Zhong, J. Zhang, A. Xia, Y. Pei, M. Chen, P. Li and M. Zhu, *J. Am. Chem. Soc.*, 2014, **136**, 15559-15565.
- 25 J. Peon, X. Tan, J. D. Hoerner, C. Xia, Y. F. Luk and B. Kohler, *J. Phys. Chem. A*, 2001, **105**, 5768-5777.
- 26 E. Tsuchida, H. Nishide, N. Shimidzu, A. Yamada, M. Kaneko and Y. Kurimura, *Makromol. Chem., Rapid Commun.*, 1981, **2**, 621-626.
- 27 S. W. Boettcher, J. M. Spurgeon, M. C. Putnam, E. L. Warren, D. B. Turner-Evans, M. D. Kelzenberg, J. R. Maiolo, H. A. Atwater and N. S. Lewis, *Science*, 2010, **327**, 185-187.
- 28 E. H. Yonemoto, G. B. Saupe, R. H. Schmehl, S. M. Hubig, R. L. Riley, B. L. Iverson and T. E. Mallouk, *J. Am. Chem. Soc.*, 1994, **116**, 4786-4795.
- 29 A. M. Fajardo and N. S. Lewis, *Science*, 1996, **274**, 969-972.
- 30 L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D.-e. Jiang and O. M. Bakr, *J. Am. Chem. Soc.*, 2015.
- 31 N. Enkin, E. Sharon, E. Golub and I. Willner, *Nano Lett.*, 2014, **14**, 4918-4922.
- 32 J. R. J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Third Edn edn., Springer Science+Business Media, Singapore, 2006.
- 33 S. Bhattacharyya and A. Patra, *Bull. Mater. Sci.*, 2012, **35**, 719-725.
- 34 C. Baslak, M. Kus, Y. Cengeloglu and M. Ersoz, *J. Lumin.*, 2014, **153**, 177-181.
- 35 P. Y. Cheng, D. Zhong and A. H. Zewail, *J. Chem. Phys.*, 1996, **105**, 6216-6248.
- 36 A. O. El-Ballouli, E. Alarousu, M. Bernardi, S. M. Aly, A. P. Lagrow, O. M. Bakr and O. F. Mohammed, *J. Am. Chem. Soc.*, 2014, **136**, 6952-6959.
- 37 S. M. Aly, S. Goswami, Q. A. Alsulami, K. S. Schanze and O. F. Mohammed, *J. Phys. Chem. Lett.*, 2014, **5**, 3386-3390.
- 38 O. F. Mohammed and E. Vauthey, *J. Phys. Chem. A*, 2008, **112**, 5804-5809.
- 39 O. F. Mohammed, *J. Phys. Chem. A*, 2010, **114**, 11576-11582.
- 40 S. M. Aly, M. R. Parida, E. Alarousu and O. F. Mohammed, *Chem. Comm.*, 2014, **50**, 10452-10455.
- 41 M. Pelton, Y. Tang, O. M. Bakr and F. Stellacci, *J. Am. Chem. Soc.*, 2012, **134**, 11856-11859.
- 42 J. Sun, W. Yu, A. Usman, T. T. Isimjan, S. Dgobbo, E. Alarousu, K. Takanabe and O. F. Mohammed, *J. Phys. Chem. Lett.*, 2014, **5**, 659-665.
- 43 T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617-2619.
- 44 D. M. Togashi and S. M. B. Costa, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1141-1150.
- 45 J. L. Dempsey, J. R. Winkler and H. B. Gray, *Dalton Trans.*, 2011, **40**, 10633-10636.