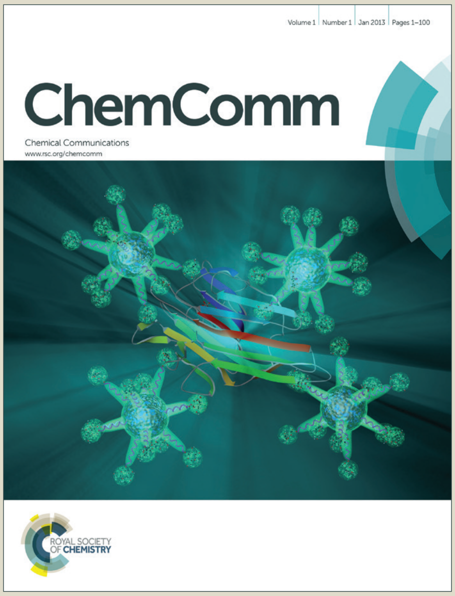
ChemComm

Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications

www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gold nanoparticles as electron reservoir redox catalysts for the 4-nitrophenol reduction: strong stereoelectronic ligand influence

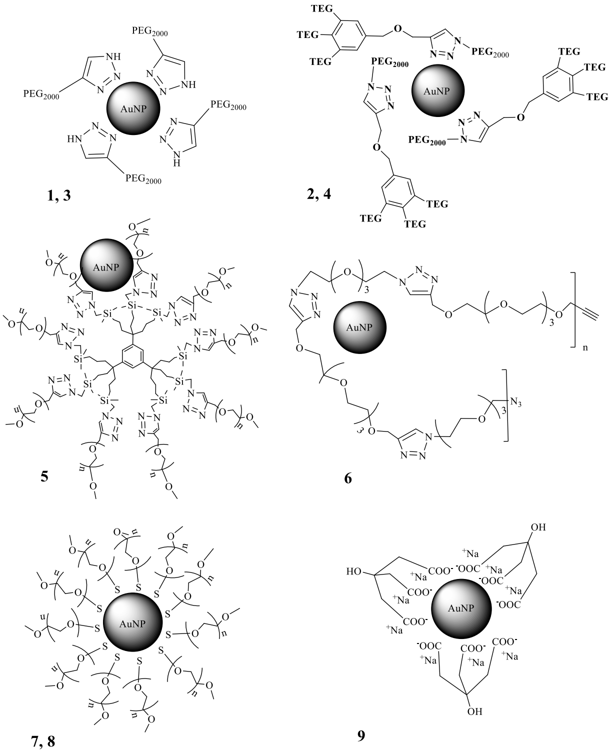
Roberto Ciganda,[a,b] Na Li,[a] Christophe Deraedt,[a] Sylvain Gatard,[a] Pengxiang Zhao,[a,c] Lionel Salmon,[d] Ricardo Hernández,[b] Jaime Ruiz[a] and Didier Astruc[a*]

The stereoelectronic properties of the stabilizing ligands of gold nanoparticles (AuNPs) are shown to play a considerable role in their catalytic efficiency for the 4-nitrophenol reduction by $NaBH_4$, consistent with a mechanism involving restructuration of the AuNP surface that behaves as an "electron reservoir".

Gold nanoparticles (AuNPs) have recently received considerable interest in a variety of applications owing to their unique physical and chemical properties.[1] In particular, extensive use in catalysis[2] has followed the seminal discoveries of low-temperature CO oxidation by small AuNPs by Haruta.[3] Among the transition metal-catalyzed redox reactions, the reduction of nitroaromatics is one of the most crucial ones.[4] Indeed, 4-nitrophenol (4-NP) is anthropogenic, toxic and inhibitory in nature. Its reduction product, 4-aminophenol (4-AP), finds applications as a photographic developer of black and white films, corrosion inhibitor, dying agent, precursor for the manufacture of analgesic and antipyretic drugs, and in particular intermediate for the synthesis of paracetamol.[5] Noble metal nanoparticle catalysts are widely employed for the reduction of 4-NP to 4-AP,[6-8] and this reaction, with an excess amount of $NaBH_4$, has often been used as a model reaction to examine the catalytic performance of metal NPs,[6,7] as first shown by Pal et al.[8] AuNP catalysts that have been examined so far are solid-supported AuNPs[7] or various thiolate-AuNPs. The reaction mechanism is still unknown, although Ballauf's group provided strong evidence for a process fitting the Langmuir-Hinshelwood (LH) model. This mechanism involves adsorption of both reactants on the surface of the catalyst for AuNPs or PdNPs that are immobilized on the surface of spherical polyelectrolyte brushes with an induction time caused by dynamic restructuring of the nanoparticle surface.[6c,7b,d,9] With other AuNPs, Pal's group also showed that the catalytic reaction took place at the AuNP surface.[10] Ghosh group showed that the rate constant increased with a decrease in the size of AuNPs and was proportional to the total surface area of AuNPs,[9] as in Ballauf group'studies,[11] and Liu et al. reported that surface functional groups influenced the catalytic behavior.[12] Katz suggested a completely different mechanism in which the active site was a leached gold species that was present in exceedingly small concentrations.[13] Zhang et al suggested that the borohydride salt transfered a hydride to the AgNPs in the case of TiO_2-supported AgNPs.[14] Scott's group showed that in the presence of excess borohydride salts, thiolate-AuNPs that catalyze 4-NP reduction growed to larger sizes.[15]

Here we show the dramatic influence of the stereolectronic effects of the ligand on the reaction rate, and we emphasize the electron reservoir behavior of the gold nanoparticle catalysts. Therefore, we compare, under identical conditions, the rates of the homogeneous 4-NP reduction by excess $NaBH_4$ catalyzed in water by water-soluble AuNPs stabilized by citrate, polyethyleneglycol (PEG) thiolate of different lengths, and mono, bifunctional, polymeric and dendritic 1,2,3-triazoles terminated with PEG 400 or 2000 (Figure 1). The catalytic 4-NP reduction is easily monitored via UV-vis spectroscopy by the decrease of the strong adsorption of 4-nitrophenolate anion at 400 nm, directly leading to the rate constant.[8] Isosbestic points in the spectra of the reacting mixtures demonstrate that no side reaction occurs.[6c] The various stable AuNPs that are studied have sizes around 3 nm, but larger AuNPs have also been examined for comparison (Table 1). The reduction rate has been observed, as in many preceeding cases, to be pseudo-first-order in the presence of a large molar excess of $NaBH_4$ (here 81 equiv. $NaBH_4$ per mol 4-NP per Au atom). All the apparent kinetic constants are summarized in Table 1. In order to obtain data that are independent from the surface, the rate constant ($k_1 = k_{app}/S$) was also estimated normalized to the surface (S) in the assumption of the LH mechanistic model[7b,16] (see also Table 1). The results clearly show that the best stabilizers, thiolates, provide the slowest AuNP catalysts, followed by the citrate. Citrate-AuNPs are large, but the comparison between thiolate-AuNPs and citrate-AuNPs of the same size (diameter : 13.5 nm) shows that the citrate-AuNPs are slightly less slow catalysts than the thiolate-AuNPs. The similarity of results with these two types of ligands, however, reveals a similarity of bonding to the AuNP, i.e. the citrate-AuNP bond should reflect coordination of citrate to the AuNP surface, as the thiolate-AuNP bond, in spite of the difference of electronegativity and polarizibility between these two chalcogen atoms.

All the 1,2,3-triazole (trz)-stabilized AuNPs[17] that are examined here are much more efficient catalysts than the AuNPs that are stabilized by the formally anionic thiolate and citrate ligands. This reveals the considerable advantage, in terms of catalytic reaction rates, of neutral ligands such as triazoles that form only weak coordination bonds with the AuNP surface given the impossibility of back bonding due to high-lying nitrogen π* orbitals. This weak bonding of the trz ligands, compared to the stronger bonding of thiolate and citrate ligands, is responsible for their easy displacement from the AuNP surface by substrates. It is also striking that the induction time (t_0), that usually is directly connected to the surface rearrangement on the AuNP surface,[7b,d] is only found with the thiolate-AuNPs and citrate-AuNPs.



1, 3 **2, 4** **5** **6** **7, 8** **9**

Fig 1. Various AuNPs under study. See the diameters (D) in Table 1. The ligands of **7** and **8** are resp. HS-PEG400 and HS-PEG2000.

Table 1. Catalytic AuNP activity in the reduction of 4-NP at 20ºC.

AuNPs stabilized	D (nm)	k_{app} (s^{-1})	t_0 (s)	k_1 ($L\ s^{-1}m^{-2}$)	Ea (KJ mol^{-1})
1	3	fast*	0	-	24
2	3	fast**	0	-	29
3	6	$1.4x10^{-2}$	0	$4.3x10^{-2}$	37
4	6	$6.7x10^{-3}$	0	$2x10^{-2}$	40
5	3.5	$7.5x10^{-3}$	0	$1.2x10^{-2}$	-
6	3.6	$1.1x10^{-2}$	0	$1.9x10^{-2}$	-
7	3.5	$7x10^{-4}$	900	$1x10^{-3}$	132
8	13.5	$4x10^{-4}$	2100	$3x10^{-3}$	-
9	13.5	$6x10^{-4}$	1200	$4x10^{-4}$	-

* At 13ºC : $k_{app} = 1.2x10^{-2}\ s^{-1}$, $k_1 = 1.7x10^{-2}\ L\ s^{-1}m^{-2}$
** At 13ºC : $k_{app} = 9.6x10^{-3}\ s^{-1}$, $k_1 = 1.4x10^{-2}\ L\ s^{-1}m^{-2}$

With these ligands, they are rather long, and by contrast, under these conditions, no induction times are found for all the trz-AuNPs, confirming the very facile trz displacement by the substrates. Among the trz-AuNPs, the dendrimer-stabilized trz-AuNPs are the less efficient catalysts. The polymer-stabilized trz-AuNPs are more efficient than the related dendrimer-stabilized trzAuNPs, but less so than the non-dendritic mono- and disubstituted trz ligands. Thus, it appears that this order of catalytic efficiency of the trz-AuNPs is related to their steric effects, the largest steric bulk being provided by the dendrimer framework that is bulkier than that of the polymer, whereas the less bulky non-macromolecular trz ligands provide by far the most efficient AuNP catalysts. These two AuNPs catalyze reactions that are so fast, under the same conditions as the other liganded AuNP catalysts, that they are too fast to observe a measurable rate at 25°C. It is possible to compare these two AuNP catalysts, however, at lower temperatures. Then the monosubstituted trz-AuNPs appear to be more efficient than the bulkier disubstituted trz-AuNPs, as expected.

These results confirm that ligand displacement by substrate on the AuNP surfaces is the dominant feature of the mechanism that involves restructuration of the surface. This is in accord with the mechanis proposed by Ballauff and others following the LH kinetic model, which in particular also discards a leaching mechanism. With the series of trz-AuNPs, it also appears that diffusion of substrates towards the trz-AuNP shows the filtration effect of the dendrimer and polymer frameworks, because the order of reaction rates follows the order of steric bulk of the trz-containing frameworks.

These data also confirm that the AuNPs play the role of an inner-sphere redox catalyst,[18] because BH_4^- tranfers a hydride to the AuNP surface, resulting in the formation of a covalent Au-H bond.[7d] This means that the negative charge is transferred to the AuNP, as already suggested,[7d,19] charge delocalization being largely facilitated by the low-lying conduction band of the AuNP. Indeed, addition of $NaBH_4$ to the trz-AuNPs leads to color change corresponding to a blue shift of the surface plasmon band (SPB) that indicates the accumulation of several negative charges at the AuNP surface. Such as shift that has been already observed in particular with thiolate AuNPs is shown here with trz-AuNPs (Fig. 2).

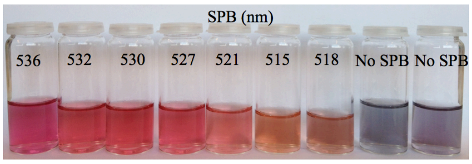


Fig. 2. Trz-AuNPs **3** after addition from left to right of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.5 and 2 equiv. of $NaBH_4$ per gold atom. The blue shift upon $NaBH_4$ addition is emphasized by values of λ_{max} (SPB).

This effect is accompanied by another effect, AuNP aggregation, i.e. AuNP size increase (Ostwald ripening),[20] upon $NaBH_4$ addition, that is characterized by a red shift of the SPB. After observation of the blue shift upon $NaBH_4$ addition, this red shift appears upon addition of more $NaBH_4$. Gold precipitation then occurs when the amount of added $NaBH_4$ becomes too high (Fig. 2).

The accumulation of negative charges at the AuNP surface proceeds along with the Au-H bond formation until the resulting electrostatic effect becomes too important. Along this line, electrochemical experiments conducted by Quinn's group by differential pulse voltammetry with well-defined thiolate-Au_{147}NP showed a series of 15 electrochemically and chemically reversible single electron transfer steps with Coulomb blockades (only limited by the electrochemical window) leading to stable multiply charged AuNPs.[21] In the presence of nitrophenolate anions on the AuNP surface, the electrochemical peak spacing that corresponds to the quantized capacitance charging was found be decrease compared to that obtained in its absence, which corresponds to a small decrease of the AuNP capacitance.[22] This shows that the AuNPs behave as "electron reservoirs".[23] This role is efficiently fulfilled by the AuNP redox catalysts for 4-NP reduction in the transformation of inner-sphere single electron transfers from borohydride ions to the surface into a multi-electron transfer. A multi-electron transfer is necessary for each 4-NP reduction to 4-AP. The citrate anions, as hydrides, form coordination bonds with the AuNP surface involving partial charge transfer from the ligand to the AuNP surface. Such as coordination with a tripod of dihapto carboxylates that are coordinated to Au (111) is known,[24] although the degree of AuNP-O covalency and charge transfer has not been addressed.

In conclusion, the role of the stabilizing ligands in the AuNP catalyzed 4-NP reduction has been shown here to be crucial. It is involved both in the restructuration at the AuNP surface following the LH kinetic model with considerable variation of efficiency from "anionic" thiolate or citrate ligands to neutral trz ligands and the steric or filtering effect[25] of the substrate through the bulk of the trz ligand framework. The difficulty to exchange the thiolate ligands does not inhibit Suzuki-Miyaura cross carbon-carbon coupling reactions with analogous PdNPs,[26a] because a leaching mechanism is involved.[26b] On the other hand, it considerably slows down AuNP-catalyzed 4-NP reduction in contrast with the situation involving easily exchanged trz ligands.[17] The data and apparent accumulation of several negative charges in the AuNPs that occurs while the Au-H bonds form upon $NaBH_4$ reaction emphasizes the role of "electron reservoirs" of these redox catalysts. Well-known precedents are found for instance in the role of PtNPs as redox catalysts in water photosplitting.[27] These finding should significantly contribute to shed light on the surface mechanism and optimize the design of effective catalysts for this intensively searched "green" aqueous reaction.

Financial support from Gobierno Vasco (R. C., post-dotoral scholarship), Universidad del País Vasco, Chinese Scholarship Council (N. L., Ph.D. grant), Ministère de la Recherche et de la Technologie (C. D., PhD grant), the CNRS (S. G. delegation), and the University of Bordeaux is gratefully acknowledged.

Notes and references

[a] Univ. Bordeaux, ISM, UMR 5515, 33405 Talence Cedex, France.
[b] Facultad de Química de San Sebastian, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastian, Spain.
[c] Science and Technology on Surface Physics and Chemistry Laboratory, PO Box 718-35, Mianyang 621907, Sichuan, China.
[d] LCC UPR 241, 205 Route de Narbonne, 31077 Toulouse Cedex, France
Email: d.astruc@ism.u-bordeaux.fr

† Electronic Supplementary Information (ESI) available: [UV-vis. spectra of the reduction of 4-NP by AuNPs, the corresponding plots of $-\ln(C_t/C_0)$ as a function of the time and $\ln k_{app}$ vs. 1/T and AuNPs synthesis and caracterizations]. See DOI: 10.1039/c000000x/

1. (a) M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; (b) X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891; (c) Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem., Int. Ed.,* 2009, **48**, 60; (d) *Gold Nanoparticles for Physics, Chemistry, Biology*, eds. C. Louis and O. Pluchery, Imperial College Press, 2012.
2. (a) M. Haruta and M. Date, *Appl. Catal. A*, 2001, **222**, 227; (b) F. Porta, L. Prati, M. Rossi and G. Scari, *J. Catal*., 2002, **210**, 464; (c) M. Haruta, *Nature*, 2005, **437**, 1098; (d) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362; (e) C. D. Pina, E. Falletta, L. Prati, M. Rossi, *Chem. Soc. Rev.*, 2008, **37**, 2077; (f) A. Corma and H. Hermenegildo, *Chem. Soc. Rev.*, 2008, **37**, 2096; (g) A. Corma, A. Leyva-Perez and J. Maria Sabater, *Chem. Rev.*, 2011, **111**, 1657; (h) N. Dimitratos, J. A. Lopez-Sanchez and G. J. Hutchings, *Chem. Sci*., 2012, **3**, 20.
3. (a) M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett*., 1987, 405; (b) M. Haruta, N. Yamada, T. Kobayashi and S. Ijima, *J. Catal*., 1989, **115**, 301; (c) M. Haruta, *Catal. Today*, 1997, **36**, 153; (d) M. Haruta, *Angew. Chem., Int. Ed*., 2014, **53**, 52.
4. A. Corma and P. Serna, *Science*, 2006, **313**, 332.
5. (a) Woo, Y.-T. and Lai, D. Y. *Aromatic Amino and Nitro–Amino Compounds and Their Halogenated Derivatives*. *Patty's Toxicology*, pp. 1–96. Wiley, New York, 2001; (b) S.C. Mitchell and R.H. Waring, "*Aminophenols*." In *Ullmann's Encyclopedia of Industrial Chemistry*, 2002 Wiley-VCH.
6. (a) A. Gangula, R. Podila, R. M. L. Karanam, C. Janardhana, A. M. Rao, *Langmuir*, 2011, **27**, 15268-15274, (b) Y. Zhang, X. Cui, F. Shi, Y. Deng, *Chem. Rev*., 2012, **112**, 2467-2505; (c) P. Herves, M. Perez-Lorenzo, L. M. Liz-Marzán, J. Dzubiella, Y. Lu, M. Ballauff, *Chem. Soc. Rev.*, 2012, **41**, 5577-5587; (d) N. C. Antonels and R. Meijboom, *Langmuir*, 2013, **29**, 13433-13442.
7. (a) K. Kuroda, T. Ishida and M. Haruta, *J. Mol. Cata. A: Chem.*, 2009, **298**, 7-11; (b) S. Wunder, F. Polzer, Y. Lu, and M. Ballauff, *J. Phys. Chem. C*, 2010, **114**, 8814-8820. (c) S.-N. Wang, M. -C. Zhang, and W. Q. Zhang, *ACS Catal*., 2011, **1**, 207-211. (d) S. Wunder, Y. Lu, M. Albrecht and M. Ballauff, *ACS Catal*., 2011, **1**, 908-916. (e) J. Li, C. -Y. Liu, and Y. Liu, *J. Mater. Chem*., 2012, **22**, 8426-8430. (f) J. Zhang, D. Han, H. Zhang, M. Chaker, Y. Zhao and D. Ma, *Chem. Commun.*, 2012, **48**, 11510-11512. (g) A. Shivhare, S. J. Ambrose, H. Zhang, R. W. Purves and R. W. J. Scott, J. *Chem. Commun.*, 2013, 49, 276-278; (h) P. Pachfule, S. Kandambeth, D. Dıaz and R. Banerjee, *Chem. Commun.*, 2014, **50**, 3169.
8. N. Pradhan, A. Pal and T. Pal, *Colloid Surf. A*, 2002, **196**, 247–257.
9. S. Panigrahi, S. Basu, S. Praharaj, S. Pande, S. Jana, A. Pal, S.K. Ghosh and T. Pal, *J. Phys. Chem. C*, 2007, **111**, 4596.
10. S. Saha, A. Pal, S. Kundu, S. Basu, T. Pal, *Langmuir*, 2010, **26**, 2885–2893.
11. Y. Mei, G. Sharma, Y. Lu, M. Drechsler, T. Irgang, R. Kempe and M. Ballauff, *Langmuir*, 2005, **21**, 12229–12234.
12. (a) W. Liu, X. Yang and W. Huang, *J. Colloid Interface Sci*., 2006, **304**, 160; (b) W. Liu, X. Yang and L. Xie, *J. Colloid Interface Sci*., 2007, **313**, 494.
13. M. M. Nigra, J.-M. Ha and A. Katz, *Catal. Sci. Technol*., 2013, 3, 2976-2983.
14. H. Zhang, X. Li and G. Chen, *J. Mater. Chem*., 2009, **19**, 8223–8231.
15. M. Dasog, W. Hou, and R. W. J. Scott, *Chem. Commun*., 2011, **47**, 8569-8571.
16. S. Panigrahi, S. Basu, S. Praharaj, S. Pande and S. Jana, A. Pal, *J. Phys. Chem. C*, 2007, **111**, 4596-4605.
17. (a) D. Astruc, L. Liang, A. Rapakousiou and J. Ruiz, *Acc. Chem. Res*., 2012, **45**, 630-640; (b) D. Astruc, *Nat. Chem.*, 2012, **4**, 255-267.
18. H. Taube, H. Myers and R. L. Rich, *J. Am. Chem. Soc*., 1953, **75**, 4118; (b) J.-M. Savéant, *Acc. Chem. Rev.*, 1980, **13**, 25; (c) J.-M. Lehn, *Science*, 1985, **227**, 849; (d) D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, VCH, New York, 1995, Chap. 7, pp. 479-506.
19. (a) P. Mulvaney, Langmuir, 1996, **12**, 788-800; (b) M. Brust, C. Kiely, *Colloïd Surf. A: Physicochim. Eng. Asp.*, 2002, **202**, 175-186.
20. (a) W. Ostwald, *Zeitschrift Phys. Chem*., 1897, **22**, 289-330; (b) N. G. Bastus, J. Comenge and V. Puntes, *Langmuir*, 2011, **27**, 11098-11105.
21. B. M. Quinn, P. Lijeroth, V. Ruiz, T. Laaksonen and K. Kontturi, *J. Am. Chem. Soc*., 2003, **125**, 6644-6645.
22. S. Chen and K. Huang, *Langmuir*, 2000, **16**, 2014-2018.
23. J.-R. Hamon, D. Astruc and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 758-766; (b) C. Ornelas, J. Ruiz, C. Belin and D. Astruc, *J. Am. Chem. Soc*., 2009, **131**, 590-601.
24. (a) S. Floate, M. Hosseini, M. R. Arshadi, D. Ritson, K. L. Young and R. J. Nichols, *J. Electroanal. Chem*., 2003, **542**, 67-71 ; (b) Y. Lin, G.-B. Pan, G.-J. Su, X.-H. Fang, L.-J. Wan and C.-L. Bai, *Langmuir*, 2003, **19**, 10000-10003.
25. (a) R. M. Crooks, Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res*. 2001, **34**, 181-190 ; (b) V. S. Myers, M. W. Weier, E. V. Carino, D. F. Yancey and R. M. Crooks, Chem. Sci. 2011, **2**, 1632-1646.
26. (a) F. Lu, J. Ruiz and D. Astruc, *Tetrahedron Lett.*, 2004, 9443-9445; (b) A. Diallo, C. Ornelas, L. Salmon, J. Ruiz and D. Astruc, *Angew. Chem., Int. Ed*., 2007, **46,** 8644-8648.
27. (a) J.-M. Lehn and J.-P. Sauvage, *Nouv. J. Chim*. 1977, **1**, 449-51 ; (b) A. Hagfeldt, M. Grätzel, Chem. Rev. 1995, **95**, 49-68.