Ion-Pair Formation of [Co^{III}(pn)$_2$(Cl)(L)$^{2+}$····· I$^−$] by Aqueous-Organic Solvent Medium Enhanced Photoreduction: A Perspective Regression Analysis

L. Devaraj Stephen[*],[iD], S.G. Gunasekaran[iD] and M. Soundarrajan[iD]

Department of Chemistry, SRM Valliammai Engineering College (Autonomous), SRM Nagar, Kattankulathur, Chengalpattu-603203, India

*Corresponding author: E-mail: stephenudt@gmail.com

Reduction of Co^{III} centre in Co^{III}(pn)$_2$(Cl)(L)$^{2+}$ with reference to solvent medium and structure of the complex *via* ion pair charge transfer (IPCT) paves way for the novel reaction mechanism route. In this work, we prepared, characterized and photoinduced the complexes Co^{III}(pn)$_2$(Cl)(L)$^{2+}$ (where L = RC$_6$H$_4$NH$_2$, R = *m*-OMe, *p*-F and H) in the presence of iodide ion. Quantum yield for 254 nm excitation of Co^{III}(pn)$_2$(Cl)(L)$^{2+}$(where L = RC$_6$H$_4$NH$_2$, R = *m*-OMe, *p*-F and H) in water-1,4-dioxane mixtures (Diox = 0, 5, 10, 15, 20, 25, and 30% (v/v)) were also derived for all the complexes in presence of added iodide ion, in which Co^{III} was reduced *via* [Co^{III}(pn)$_2$(Cl)(L)$^{2+}$····· I$^−$] ion-pair formation. The photoinduced state is ion-pair charge transfer transition state and the quantum efficiency is solvent reliant and they are non-reactive. That is, change in $\Phi_{Co(II)}$ is dependable with observed increase in x$_{Diox}$ of the mixed solvent medium. Correlation analysis using empirical parameters ε_r, Y, E$_T^N$ and DN^N provides a model to understand the solvent medium participation and interaction. This work gains an insight into the role of aqueous-organic solvent medium in Co^{III}(pn)$_2$(Cl)(L)$^{2+}$ photoreduction, which may be of great significance in developing novel approaches in the field of high performance catalysis.

Keywords: Ion Pair charge transfer, Cobalt(III) complex, 1,4-Dioxane, Solvation, Regression analysis, Photoreduction.

INTRODUCTION

The tremendous advantage of photochemical activation of transition metal complexes is the generation of electronic excited states under very moderate reaction condition. Ion pair charge transfer (IPCT) between excited material and adsorbed species [1,2]. This effect opens several possibilities to design various materials which can find environmental, biological and medical applications. Metal complexes exhibit a high level of organization and therefore, they are quite useful as components of molecular level photochemical devices. These are carefully designed to perform desired functionalities such as energy conversion, molecular sensing, labeling, switching, catalysis, hydrometallurgy and spent nuclear fuel reprocessing, *etc*. [3,4].

During the last few years special attention has been paid to the study of solvent effects on different reactions, particularly in aqueous-organic solvent medium, as it paves way for solute-solvent interaction. In pure solvents, the composition of the solvation microsphere is the same as in the bulk solvent and

it's different for aqueous-organic solvent medium. These solvent effects have generally been understood using ion pair charge transfer (IPCT). Though many earlier communications reports about the effect of solvent on various types of reactions such as substitution [5-9], redox [10-14], photo-reduction [15-17] and solvolysis [18,19] of metal complexes have been published, such solvent variation studies on the aryl complexes with IPCT are very occasional.

Great efforts have been paid on improving present methods to investigate the synthesis, spectral characterization and solvent effects on the photoreduction of a series of Co^{III}(pn)$_2$(Cl)(L)$^{2+}$(where L = RC$_6$H$_4$NH$_2$, R = *m*-OMe, *p*-F and H) in binary aqua-organic solvent media. The solvent effects on the reaction have been carried out in water/1,4-dioxane mixtures of varying compositions and correlation analysis of the data was carried out using linear free energy relationships for the proper understanding of the mechanism. The selection of the organic co-solvents for the study is based on the fact 1,4-dioxane is a typical non-HBD solvent. Hence by varying the concentration of these solvents in the binary aqua-organic solvent

medium, the hydrogen bonding properties of the mixture can be diverse smoothly.

EXPERIMENTAL

Cobalt(III) aryl-amines were prepared according to the reported method [20,21] and the purity of the complexes was checked with UV-visible data reported earlier [21]. AnalarR grade methanol and KI were purchased from E-Merck. Binary solvent mixtures with the ratio of 0, 5, 10, 15, 20, 25 and 30% (v/v) of organic co-solvent (*i.e.* methanol/1,4-dioxane) in aqueous-organic solvent medium . The ionic strength was adjusted to 0.1 M with A.R. grade $NaNO_3$. All irradiated solutions were freshly prepared and thermostated to 293 and 300 K. The $Co^{III}(pn)_2(Cl)(L)^{2+}$ concentration was generally 2.54×10^{-3} to 5.69×10^{-3} M and photolysis was carried out in dim red light. Solvent mixtures were prepared by volume percent and conversion of mole fraction of the co-solvent (x_2) was made using density data.

RESULTS AND DISCUSSION

The complex $Co^{III}(pn)_2(Cl)(L)^{2+}$ (where L = $RC_6H_4NH_2$, R = *m*-OMe, *p*-F and H) is less reactive upon 254 nm irradiation but reacts well in presence of iodide ion. The UV-visible spectra recorded during photolysis of $Co^{III}(pn)_2(Cl)(L)^{2+}$ showed the persistent shifting of the peaks. The electronic absorption of the complex showed a blue shift at $\lambda_{max} \approx 300$ nm upto 3.86-3.94, 3.89-3.98 and 3.90-3.99 nm for *m*-OMe, *p*-F and H complexes, respectively. The photoreduction of Co^{III} into Co^{II} was followed through repetitive scan spectra recorded, and the spectral changes observed upon 254 nm photolysis *trans-*$[Co^{III}(pn)_2Cl(C_6H_5NH_2)]Cl_2$ in 10% 1,4-dioxane mixtures as a utility of irradiation time at 27 ℃ is shown in Fig. 1. At the time of irradiation for regular intervals, blenching of solution took place with a related increase in absorbance [22] at 350 nm representing I_3^- absorption. The characteristic spectral absorptions at 625 nm for $Co^{II}(NCS)_4^{2-}$ and 475 nm for I_3^- specifies the reduction of cobalt(III) center by iodide ion into Co^{II} and iodine radical. The study ascribed that the photoreduction is due to ion-pair charge transfer (IPCT) state, such absorptions are generally observed for {Co(III) and I^-} systems. The quantum yields of $\Phi_{Co(II)}$ increase with the increase in the aqueous-organic solvent medium content as with the decrease in the polarity charge in the mixed solvent medium, the equilibrium constant of ion-pair formation have the increasing trend [23,24]. A suitable regression analysis can establish the complexity and contribution of medium on photoreactions *via* ion-pair formation. Table-1 shows the net photoreaction observed
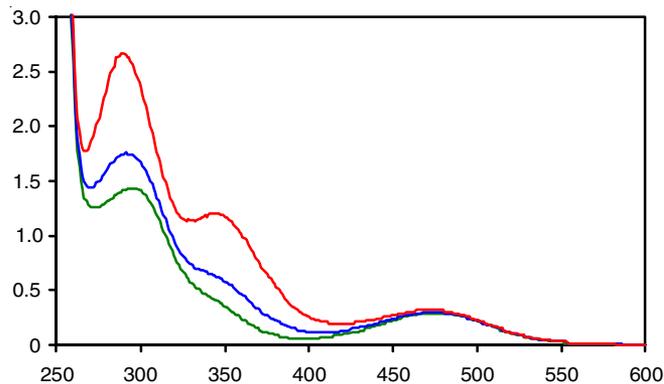
Fig. 1. Photoreduction of $[Co^{III}(pn)_2Cl(C_6H_5NH_2)]Cl_2$ at water-methanol mixtures at 0, 120 and 240 s at 254 nm irradiation

in binary solutions at their natural pH (~ 6.7). The quantum yield increases with the increase in the methanol/1,4-dioxane concentration in the irradiated solution [25]. It indicates that the population of 1,4-dioxane molecules in the solvation area increases considerably with the increase in the cosolvent content, x_{Diox}. Fig. 2 present a linear relationship of log $\Phi_{Co(II)}$ at two different temperatures with mole fraction of 1,4-dioxane, x_2 = 0.0229 to 0.1602.
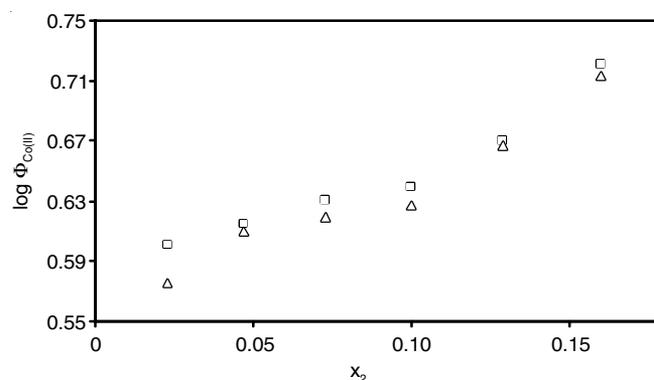
Fig. 2. Plot of log $\Phi_{Co(II)}$ *versus* x_2 for the photoreduction of $Co^{III}(pn)_2Cl(RC_6H_4NH_2)]Cl_2$ complex at 293 K (□) and 300 K (△) in water-1,4-dioxane mixtures in the presence of iodide ion

Variation of quantum yield with $1/\varepsilon_r$: Fig. 3 illustrate a linear plot of log $\Phi_{Co(II)}$ *versus* the reciprocal of relative permittivity (ε_r^{-1}). The Laidler-Eyring equation can be applied by least-squares procedure for the linearity in its medium [26]. The correlation analysis of Co(III)-mixed solvent medium are given in Table-2. To assess the implication of relative permittivity in the photoreduction of $[Co^{III}(pn)_2Cl(C_6H_5NH_2)]Cl_2$ in water-1,4-dioxane (293K) (eqn. 1) and 300K (eqn. 2), regression analysis was carried out with $1/\varepsilon_r$.

TABLE-1
QUANTUM YIELDS FOR THE PHOTO REDUCTION OF $Co^{III}(pn)_2Cl(RC_6H_4NH_2)]Cl_2$ IN AIR EQUILIBRATED WATER-1,4-DIOXANE MIXTURES AT DIFFERENT TEMPERATURES. IRRADIATION WAVELENGTH-254 nm WITH IODIDE ION

R in aniline	Temp. (K)	x_2	$\Phi_{Co(II)} \times 10^{-1}$; 1,4-dioxane % (v/v)						
			0	5	10	15	20	25	30
m-OMe	293	0.0365	3.86	3.51	3.84	4.02	4.19	4.58	4.93
	300		3.94	3.76	4.07	4.16	4.24	4.64	5.17
p-F	293	0.1422	3.89	3.84	3.88	4.09	4.26	4.83	5.26
	300		3.98	3.97	4.12	4.21	4.39	4.89	5.34
H	293	0.1632	3.90	3.76	3.72	3.97	4.20	4.78	5.38
	300		3.99	3.88	4.08	4.18	4.28	5.14	5.52

TABLE-2
STATISTICAL RESULTS OF THE LAIDLER-EYRING'S EQUATION FOR THE PHOTOREDUCTION OF
$[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ ION IN WATER-1,4-DIOXANE MIXTURES AT DIFFERENT TEMPERATURES

R in aniline	Temp. (K)	r^2	sd	Ψ	X	I
m-OCH₃	293	0.9860	0.0070	0.130	30.617	0.1429
	300	0.9521	0.0118	0.240	27.425	0.2094
p-F	293	0.9590	0.0124	0.222	31.221	0.1517
	300	0.9593	0.0111	0.221	28.034	0.2143
H	293	0.9456	0.0166	0.255	35.899	0.0722
	300	0.9241	0.0188	0.302	34.111	0.1212

r^2 = Correlation coefficient; sd = Standard deviation; Ψ = Exner's statistical parameter
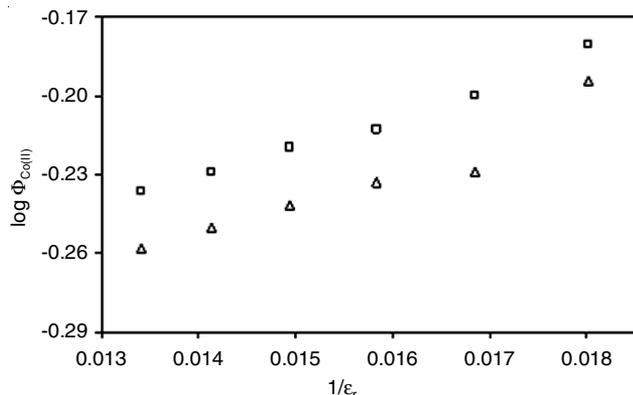
Fig. 3. Plot of log $\Phi_{Co(II)}$ *versus* $1/\varepsilon_r$ for the photoreduction of $Co^{III}(pn)_2Cl(RC_6H_4NH_2)]Cl_2$ complex in water-1,4-dioxane mixtures at two different temperatures

Fig. 4. Plot of log $\Phi_{Co(II)}$ *versus* Y for the photoreduction of $Co^{III}(pn)_2Cl(RC_6H_4NH_2)]Cl_2$ complex in water-1,4-dioxane mixtures at two different temperatures in the presence of iodide ion

$$\log \Phi_{Co(II)} = 0.0722 + 35.899 \; 1/\varepsilon_r \qquad (1)$$
($r^2 = 0.9456$, sd = 0.0166, ψ = 0.255, n = 6 and Temp. = 293 K)

$$\log \Phi_{Co(II)} = 0.2143 + 28.034 \; 1/\varepsilon_r \qquad (2)$$
($r^2 = 0.9241$, sd = 0.0188, ψ = 0.302, n = 6 and Temp. = 300 K)

Parameter of solvent assets: The Grunwald-Winstein relationship [27,28] by log k = log kₒ + mY, (where k and k₀ are replaced by ψ_Co(II) and ψ°_Co(II)) was attempted towards regression analysis and K (rate constant) stands for a compound in a solvent and k₀in the standard solvent and m is the solvent parameter measuring compassion of reaction rate towards Y. Fig. 3 shows the linearity in the arrival of Grunwald-Winstein relationship. For the present system it was understood that the linearity of the plots in Fig. 4, which ensures the major role of discrete molecular structure and the $\Phi_{Co(II)}$ controls the initial transition to that of transition state towards differential salvation with various solvent composition. Lappin *et al.* [29] proved that solvent dielectric selectivity in the reduction of a series of cobalt(III) complexes in aqueous solutions for mixed ligands. The complex

$Co^{III}(pn)_2(Cl)(L)^{2+}$ forms a tighter ion-pair with I⁻ ion in the lower relative permittivity medium and this tighter structure was well stabilized in a mixture containing higher mole fraction of 1,4-dioxane ($x_2 = 0.2750$). Relative permittivity is a suitable measure of long range medium effects on reactions [30,31]. The stabilization of the excited state depends on the formation of hydrogen bonds with the ability of the protic solvents.

Photoreduction yield in the presence of iodide ion increases with the decrease in polarity of the medium suggests that the excited state is less polar than the ground state. In Fig. 3, the lines showed a negative slope values indicated that the quantum yield depends on the solvation structural contribution. Thus, considerable charge separation takes place in the ion-pair, $[Co^{III}(pn)_2(Cl)(L)^{2+}·····I^-]$, leading to solvent caged radical pair, $[Co^{III}(pn)_2(Cl)(L)^{2+}·····I^·]$ due to effective solvation.

Fig. 4 is a plot of log $\Phi_{Co(II)}$ *versus* Y (Grunwald-Winstein polarity parameter), corresponding to $Co^{III}(pn)_2Cl(RC_6H_4NH_2)]Cl_2$ photoreduction in water-1,4-dioxane (293 K) (eqn. 3)/(300 K) (eqn. 4). The analysis results are shown in Table-3.

TABLE-3
STATISTICAL RESULTS, THE COEFFICIENTS AND WEIGHTED CONTRIBUTIONS OF SOLVENT PARAMETERS FROM
GRUNWALD-WINSTEIN EQUATION FOR THE PHOTOREDUCTION OF $[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ ION COMPLEXES IN
WATER-1,4-DIOXANE MIXTURES AT DIFFERENT TEMPERATURES WITH IODIDE ION

R in aniline	Temp. (K)	r^2	sd	Ψ	X	I
m-OCH₃	293	0.9872	0.0067	0.124	-0.1548	1.0729
	300	0.9470	0.0124	0.252	-0.1382	1.0411
p-F	293	0.9522	0.0134	0.239	-0.1572	1.0981
	300	0.9522	0.0120	0.239	-0.1411	1.0640
H	293	0.9370	0.0178	0.275	-0.1806	1.1599
	300	0.9173	0.0196	0.315	-0.1718	1.1551

r^2 = Correlation coefficient; sd = Standard deviation; Ψ = Exner's statistical parameter

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TABLE-4

STATISTICAL RESULTS, THE COEFFICIENTS AND WEIGHTED CONTRIBUTIONS OF SOLVENT PARAMETERS
FROM KRYGOWSKI-FAWCETT EQUATION FOR THE PHOTOREDUCTION OF $[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ ION
COMPLEXES IN WATER-1,4-DIOXANE MIXTURES AT DIFFERENT TEMPERATURES WITH IODIDE ION

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R in aniline	Temp. (K)	Statistical parameters						
		R^2	sd	Ψ	a	b	$P(E_T^N)$	$P(DN^N)$
		$Q = Q_o + \alpha E_T^N + \beta DN^N$						
m-OMe	293	0.996	0.006	0.078	-0.03	-4.09	1	99
	300	0.981	0.009	0.169	1.57	-10.70	13	87
p-F	293	0.976	0.011	0.192	1.79	-12.16	13	87
	300	0.993	0.005	0.104	1.93	-12.38	1	99
H	293	0.982	0.011	0.164	2.38	-15.45	13	87
	300	0.962	0.015	0.240	2.47	-15.59	14	86

R^2 = coefficient of multiple determination; sd = standard deviation; Ψ = Exner's statistical parameter; a and b – coefficients of E_T^N and DN^N eq;
$P(E_T^N)$ and $P(DN^N)$ – weighted percentage contributions.

$$\log \Phi_{Co(II)} = -0.1806 - 1.1599\,Y \qquad (3)$$

$(r^2 = 0.9370, sd = 0.0178, \psi = 0.275, n = 6$ and Temp. = 293 K)

$$\log \Phi_{Co(II)} = 4.258 - 0.956\,Y \qquad (4)$$

$(r^2 = 0.9173, sd = 0.0196, \psi = 0.315, n = 6$ and Temp. = 300 K)

Short range solvation effects: The specific and short-range solvation effects on excited state/ligand radical pair paves way to the extent of variation in quantum yield. In order to study the specific solvation effect interaction, biparametric equation, Krygowski-Fawcett was analyzed. The solvation effect is characterised experimentally in strong correlations of $\Phi_{Co(II)}$ and the empirical solvent parameters, such as Reichardt's E_T^N and Gutmann's DN^N, which appear to measure both micro polarity and solvent Lewis basicity, respectively. The solvent effect on $\Phi_{Co(II)}$ could be represented as: $Q = Q_0 + \alpha E_T^N + \beta DN^N$, where $Q = \log \Phi_{Co(II)}$, $Q_0 = \log \Phi^0_{Co(II)}$ and α and β are the regression coefficients. Linear solvation energy *via* mixed solvent medium shows excellent correlations with the $\Phi_{Co(II)}\{Co^{III}(pn)_2(Cl)(L)^{2+}$, $I^-\}$ association is probably significant at micro-level [32,33]. The analysis results are shown in Table-4.

Regression analysis for $Co^{III}(pn)_2Cl(RC_6H_4NH_2)]Cl_2$ is presented in eqn. 5 and 6.

$$\log \Phi_{Co(II)} = -10.005 + 2.38\,E_T^N - 15.45\,DN^N \qquad (5)$$

$(R^2 = 0.982, sd = 0.011, \psi = 0.164, n = 6$ and Temp. = 293 K)

$$\log \Phi_{Co(II)} = -8.319 + 2.47\,E_T^N - 15.59\,DN^N \qquad (6)$$

$(R^2 = 0.962, sd = 0.015, \psi = 0.240, n = 6$ and Temp. = 300 K)

The back electron transfer reactions within the mixed solvent medium predominate with IPCT. The primary photo-products due to the solvent cage effects are explained in eqns. 7-9:

$$\{[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}, I^-\} + h\nu \longrightarrow$$
$$\{[Co(pn)_2Cl(RC_6H_4NH_2)]^+, I\} \qquad (7)$$

$$\{[Co(pn)_2Cl(RC_6H_4NH_2)]^+, I\} \longrightarrow$$
$$\{[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}, I^-\} \qquad (8)$$

$$\{[Co(pn)_2Cl(RC_6H_4NH_2)]^+, I\} \longrightarrow$$
$$\{[Co^{2+}(pn)_2Cl(RC_6H_4NH_2)]^+\} + I \qquad (9)$$
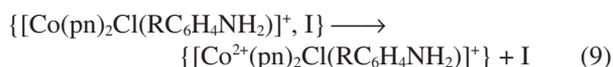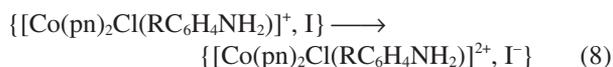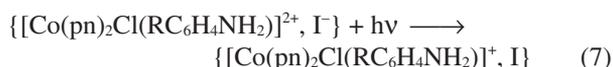
The iodine radical, $I^\bullet$, is then scavenged by I^- ions to yield I_2^-, which is able to oxidize $[Co^{2+}(pn)_2Cl(RC_6H_4NH_2)]^+$ undergoes disproportionation reaction [34].

Conclusion

An aqueous-organic solvent medium plays a major role in the resolve of quantum yield with higher x_2, a fraction of the electron transfer products that escape due to solvent cage and dissociate before they can back react. The solvent cage plays a very vital role even though its contribution towards the photoreduction is less. This is kept by the magnitude of the $\Phi_{Co(II)}$ which is associate with the reactions in neat water. The various analysis proved the solvation influence on the ion pair charge transfer. This indicates that the transition state has a lower charge density than the cobalt(III) ion confirming the iodine component of the ion-pair. Solvent cage stabilizes the excited state ion-pair $\{[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}, I^-\}$ because the electron of iodide ion was partly shifted to $\{[Co^{2+}(pn)_2Cl-(RC_6H_4NH_2)]^+\}$ ion. The solvent cage containing both water and organic cosolvent (Diox) comprises of hydrophobic ion of C_4H_8 of 1,4-dioxane. Ion pair charge transfer (IPCT) relaxation dynamics considered in this work, is of vital importance for our understanding of the photophysics and photochemistry of transition metal complexes and their building blocks as it confirms the less polarity in the hydrophobic solvent cage.

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CONFLICT OF INTEREST

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The authors declare that there is no conflict of interests regarding the publication of this article.

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REFERENCES

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1. T. Tachikawa, M. Fujitsuka and T. Majima, *J. Phys. Chem. C*, **111**, 5259 (2007);
https://doi.org/10.1021/jp069005u
2. A. Hagfeldt and M. Graetzel, *Chem. Rev.*, **95**, 49 (1995);
https://doi.org/10.1021/cr00033a003
3. A. Mills and S.J. Le Hunte, *J. Photochem. Photobiol. Chem.*, **108**, 1 (1997);
https://doi.org/10.1016/S1010-6030(97)00118-4
4. M. Gratzel, *Inorg. Chem.*, **44**, 6841 (2005);
https://doi.org/10.1021/ic0508371
5. X. Liu, J. Zhang, L. Yang and W.L. Hase, *J. Am. Chem. Soc.*, **140**, 10995 (2018);
https://doi.org/10.1021/jacs.8b04529
6. K. Anbalagan and L.D. Stephen, *Transition Met. Chem.*, **34**, 915 (2009);
https://doi.org/10.1007/s11243-009-9281-1
7. K. Anbalagan and L.D. Stephen, *Z. Phys. Chem.*, **220**, 335 (2006);
https://doi.org/10.1524/zpch.2006.220.3.335
8. T.A. Hamlin, B. van Beek, L.P. Wolters and F.M. Bickelhaupt, *Chem. Eur. J.*, **24**, 5927 (2018);
https://doi.org/10.1002/chem.201706075

9. Y. Wang, Z. Wu, H. Weng, X. Ding, L. Wang, F. Li, Y. Wei, S. Cheng, S. Yamashita and M. Lin, *J. Photochem. Photobiol. Chem.*, **380**, 111823 (2019);
https://doi.org/10.1016/j.jphotochem.2019.04.034

10. X. Yuan, L. Jiang, J. Liang, Y. Pan, J. Zhang, H. Wang, L. Leng, Z. Wu, R. Guan and G. Zeng, *Chem. Eng. J.*, **356**, 371 (2019);
https://doi.org/10.1016/j.cej.2018.09.079

11. S. Singh, I. Ahmed and K.K. Haldar, *J. Colloid Interface Sci.*, **523**, 1 (2018);
https://doi.org/10.1016/j.jcis.2018.03.012

12. L. Hou, Y. Zhang, Y. Ma, Y. Wang, Z. Hu, Y. Gao and Z. Han, *Inorg. Chem.*, **58**, 16667 (2019);
https://doi.org/10.1021/acs.inorgchem.9b02777

13. J. Chateauneuf, *Chem. Phys. Lett.*, **164**, 577 (1989);
https://doi.org/10.1016/0009-2614(89)85261-3

14. J. Ojeda, C.A. Arrell, L. Longetti, M. Chergui and J. Helbing, *Phys. Chem. Chem. Phys.*, **19**, 17052 (2017);
https://doi.org/10.1039/C7CP03337K

15. P.Z. El-Khoury and A.N. Tarnovsky, *Chem. Phys. Lett.*, **453**, 160 (2008);
https://doi.org/10.1016/j.cplett.2007.12.081

16. A.S. Mereshchenko, P.K. Olshin, A.M. Karimov, M.Yu. Skripkin, K.A. Burkov, Yu.S. Tveryanovich and A.N. Tarnovsky, *Chem. Phys. Lett.*, **615**, 105 (2014);
https://doi.org/10.1016/j.cplett.2014.10.016

17. K. Ando, *J. Phys. Chem. B*, **112**, 250 (2008);
https://doi.org/10.1021/jp074822v

18. C.T. Middleton, B. Cohen and B. Kohler, *J. Phys. Chem. A*, **111**, 10460 (2007);
https://doi.org/10.1021/jp0740595

19. A.S. Mereshchenko, O.S. Myasnikova, P.K. Olshin, S.M. Matveev, M.S. Panov, V.A. Kochemirovsky, M.Yu. Skripkin and A.N. Tarnovsky, *J. Phys. Chem. B*, **122**, 10558 (2018);
https://doi.org/10.1021/acs.jpcb.8b06901

20. J.C. Bailar Jr. and L.B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945);
https://doi.org/10.1021/ja01218a006

21. J.C. Bailer and C.L. Rollinson, *Inorg. Synth.*, **22**, 222 (1946).

22. F. Pina, M. Ciano, L. Moggi and V. Balzani, *Inorg. Chem.*, **24**, 844 (1985);
https://doi.org/10.1021/ic00200a009

23. B. Peng, H. Chao, B. Sun, H. Li, F. Gao and L.N. Ji, *J. Inorg. Biochem.*, **101**, 404 (2007);
https://doi.org/10.1016/j.jinorgbio.2006.11.008

24. A. Kumar, P.K. Prajapati, M.S. Aathira, A. Bansiwal, R. Boukherroub and S.L. Jain, *J. Colloid Interface Sci.*, **543**, 201 (2019);
https://doi.org/10.1016/j.jcis.2019.02.061

25. H. Kunkely and A. Vogler, *J. Organomet. Chem.*, **572**, 131 (1999);
https://doi.org/10.1016/S0022-328X(98)00731-1

26. E.S. Amis and J.F. Hinton, Solvent Effect on Chemical Phenomena: Academic Press, vol. 1 (1973).

27. E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948);
https://doi.org/10.1021/ja01182a117

28. I.S. Koo, J.M. Cho, S.K. An, K. Yang, J.P. Lee and I. Lee, *Bull. Korean Chem. Soc.*, **24**, 431 (2003);
https://doi.org/10.5012/bkcs.2003.24.4.431

29. T. Mitani, N. Honma, A. Tatehata and A.G. Lappin, *Inorg. Chim. Acta*, **39**, 331 (2002);
https://doi.org/10.1016/S0020-1693(01)00753-8

30. J. Lin, B. Qin and G. Zhao, *J. Photochem. Photobiol. Chem.*, **354**, 181 (2018);
https://doi.org/10.1016/j.jphotochem.2017.09.019

31. J.G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1936);
https://doi.org/10.1063/1.1749489

32. X.-L. Sun, Q.-Y. Zhu, L.-W. Qian, L. Yu, Z.-G. Ren, G.-Q. Bian and J. Dai, *Inorg. Chem. Commun.*, **46**, 130 (2014);
https://doi.org/10.1016/j.inoche.2014.05.038

33. A.C. Bowman, C. Milsmann, C.C. Hojilla Atienza, E. Lobkovsky, K. Wieghardt and P.J. Chirik, *J. Am. Chem. Soc.*, **132**, 1676 (2010);
https://doi.org/10.1021/ja908955t

34. T. Koide, I. Aritome, T. Saeki, Y. Morita, Y. Shiota, K. Yoshizawa, H. Shimakoshi and Y. Hisaeda, *ACS Omega*, **3**, 4027 (2018);
https://doi.org/10.1021/acsomega.8b00239