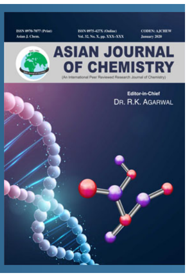
Asian Journal of Chemistry; Vol. 32, No. 9 (2020), 2139-2142

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22720



A Novel Sensor from Cyclotriveratrylene Derivative for Rapid Detection of 4-Nitrophenol Based on Fluorescence

PATRICK F. FERNANDES and DIVYA R. MISHRA*

Department of Chemistry, Gujarat University, Ahmedabad-380009, India

*Corresponding author: Tel: +91 79 26302363; E-mail: pandey.divyamishra@gmail.com

Received: 13 March 2020; *Accepted*: 9 May 2020; *Published online*: 20 August 2020; AJC-20003

In order to study various environmental pollutants among the class of nitro aromatic compounds, a new and novel sensor derived from a cyclotriveratrylene derivative has been developed which rapidly detects 4-nitrophenol from among the class of nitro aromatic compounds *via* spectrofluorimetric method. The newly derrivaritized cyclotriveratrylene compound is successfully confirmed by using the available techniques of ^{1}H NMR, ^{13}C NMR and ESI-MS. The newly developed molecule was named 4C7NbF-CTV. The complexation behaviour of 4C7NbF-CTV with various nitro aromatic compounds was studied. In the absorption spectra a shift was observed, which indicated that 4-nitrophenol interact with 4C7NbF-CTV. An enhanced intensity of fluorescence of 4C7NbF-CTV was observed on adding 4-nitrophenol.

Keywords: 4-Nitrophenol, Cyclotriveratrylene, Spectrofluorimetry, Chemosensors.

INTRODUCTION

Nitro phenols are an important class of chemical substances which have many industrial applications as intermediates as well as they are degradation products of various pesticides. Parathion is one such pesticide whose breakdown results into formation of 4-nitrophenol [1-3]. It is also an intermediate in the synthesis of paracetamol.

4-Nitrophenol as waste is found in river water [4], soil [5], atmosphere [6], fog [7] and rain [8]. It is seen that 4-nitrophenol is carcinogenic [9] and mutagenic [10]. Nitro phenol compounds are toxic to plants. They are also toxic for living beings also they give foul aroma and unsuitable tang to water if present in minute concentrations [11]. The short term exposure and inhalation of *p*-nitro phenol causes cephalgia, sleepiness, vomiting and discolouration of skin. And so with so many harmful effects of this compound, its detection and elimination from the environment is of utmost importance [12].

Many methods for the detection of nitro phenols have been proposed. Techniques such as mass spectrometry, gas chromatography, liquid extraction and capturing of electron have been accepted by the Environmental Protection Agency (EPA) [13,14]. Various other methods such as spectrophotometry [15], gas chromatography [16], HPLC [17] have been used. Among the classes of sensors, chemosensors based on luminescence have several benefits, since they are quick to detect even the slight changes. Based on these facts, chemists have shown keen interest to develop chemosensors for the detection of nitroaromatic compounds, on account of their presence in the biological environment and also the risks it posses as toxic pollutant, also, it represents a matter of worry when it is present in unchecked amount in the environment.

Therefore, with a view to develop a new cyclotriveratrylene based chemosensor, the synthesis of a new cyclotriveratrylene derivative with 4-chloro-7-nitrobenzfuran (4C7NbF) has been reported and its complexation behaviour with many nitro aromatic compounds has been shown. 4C7NbF-CTV has been successfully developed and is confirmed by ^{1}H NMR, ^{13}C NMR and ESI-MS techniques. The newly developed molecule 4C7NbF -CTV has been studied as an sensor which detects 4-nitrophenol from among the class of available nitro aromatic compounds.

Since emission intensities can be affected by many factors no particular protocol can be used for its quantitative explanation. However in the enhancement of intensities of fluorescence and also in the shift that is observed in the spectra of emission of 4C7NbF-CTV alongside of 4-nitrophenol, an explanation has been provided. Also studies of binding constants and quantum yield have been carried out further.

EXPERIMENTAL

All the chemicals and solvents were purchased from Sigma-Aldrich (India) and used without further purification. Using a VEEGO (Model; VMP-DS) melting point apparatus the melting points were measured. The ^{1}H, ^{13}C NMR spectra were recorded on a Bruker 400 MHz using TMS as an internal standard. Using a waters 2690 separatin module mass spectrometer, mass spectra were recorded. Fluoroscence measurements were measured on a Jasco Spectrofluorometer in the spectrum of 200-800 nm.

Synthesis of 4C7NbF-CTV: Cyclotriguaiacyclene (CTG) was prepared by the reaction of cyclotriveratrylene and $AlCl_3$ in MDC as per the procedure [18]. CTG (0.4 g, 0.98 mmol), K_2CO_3 (0.5 g, 0.31 mmol) were mixed with 10 mL of dry DMF followed by the addition of 4-chloro-7-nitrobenzfuran (4C7NbF) (0.58 g, 0.29 mmol) and the reaction was carried out at 150 °C for appropriate reaction time with TLC monitoring (**Scheme-I**). The reaction was allowed to rest, followed by filtration and a water wash (3 × 10 mL) and dried to yield a pure dark brown solid material. ^{1}H NMR (500 MHz, DMSO) δ: 8.14 (d, 1H), 7.27 (d, 1H), 6.78-6.70 (m, 1H), 6.68 (q, 1H), 6.46 (t, 1H), 3.92 (t, 1H), 3.89 (t, 1H), 3.88 (s, 3H), 3.84 (s, 1H), 3.67 (d, 1H); ^{13}C NMR (500 MHz, DMSO): 36.3, 56.1, 112.5, 115.7, 130.2, 134.1, 135.1, 148.2; ESI-Mass: 896.3; m.p.: > 280 °C.

Spectrofluorimetric studies: Stock solutions of 4C7NbF-CTV (0.00002 M) and nitro aromatic compounds (0.002 M) 4-nitrotoluene (4-NT); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); 1,3-dinitrobenzene (1,3-DNB); 2,3-dimethyl-2,3-dinitrobutane (DMNB); 2,4,6-trinitrotoluene (TNT); 2,4,6-trinitrophenol (TNP); 4-nitrophenol (4-NP) were prepared in acetonitrile respectively. Stock solutions (2.5 mL) of both 4C7NbF-CTV and each one of the nitro aromatic compounds respectively were taken together in the same volumetric flask, so as the concentration of 4C7NbF-CTV is 0.00001 M for the nitro compounds.

RESULTS AND DISCUSSION

Absorption and fluorescence studies of the compound 4C7NbF-CTV with the nitroaromtic compounds: The studies of ligand 4C7NbF-CTV by adding the nitro aromatic compounds *viz.* 4-nitrotoluene (4-NT); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); 2,3-dimethyl-2,3-dinitrobutane (DMNB); 2,4,6-trinitrotoluene (TNT); 2,4,6-trinitrophenol (TNP); 4-nitrophenol (4-NP) were carried out in acetonitrile. It was observed that 4-nitro phenol among the various nitro compounds displayed indicative changes as to other nitro aromatic compounds.

Further no changes were seen in the ligand 4C7NbF-CTV in presence of other nitro aromatic compounds as shown in Fig. 1. The ligand 4C7NbF-CTV showed a base peak at 470.5 nm. differences in the base peak were seen in presence of Aromatic nitro compound 4-nitrophenol and the peak at 470.5 nm was drifted to 363.5 nm. This shift showed that the compound is collaborating with 4C7NbF-CTV.

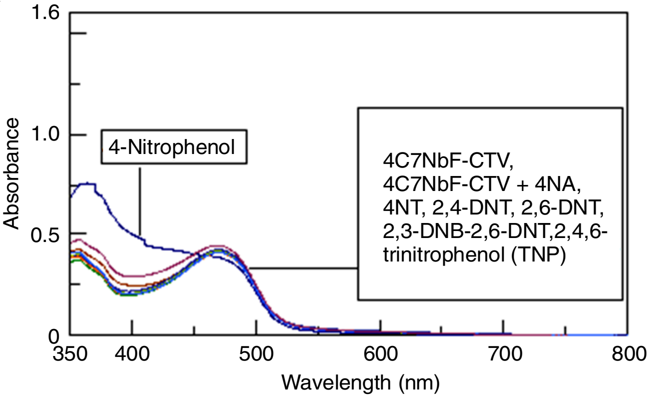
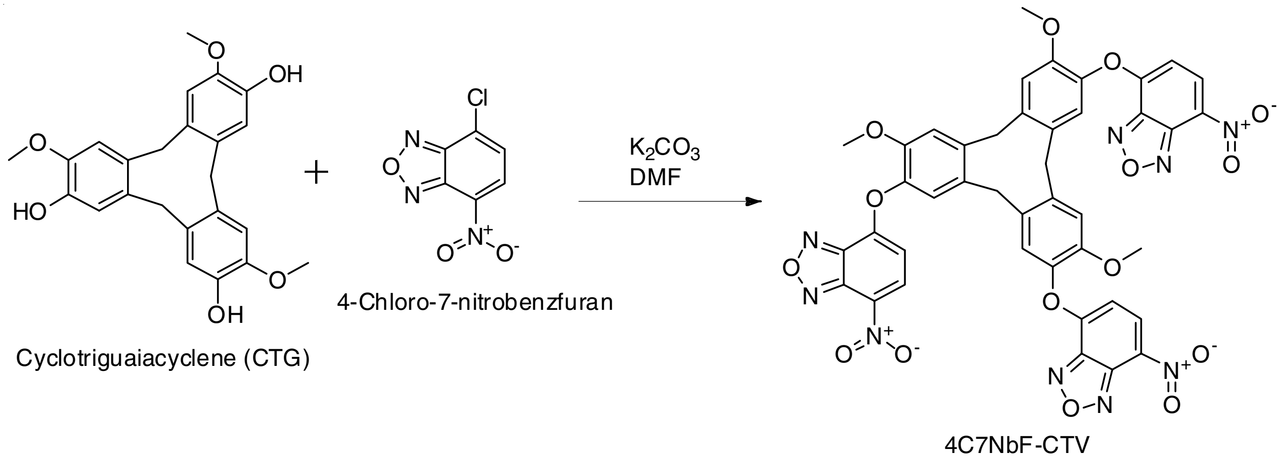


Fig. 1. Absorption spectra of upon addition of different 4NA, 4NT, 2,4DNT, 2,6-DNT, picric acid, 2,3-DNB-2, 6-DNT

As 4-nitrophenol is harmonized with oxygen atom, the higher (excited) state is more balanced *via* the ion as in to the lower (ground) state and this initiates the shifts of the peaks. Due to domination of lone pair of the oxygen atoms in the 4-chloro-7-nitrobenzfuran groups, electronic perturbation mechanics is involved by the synching of 4C7NbF-CTV with the 4-nitrophenol atoms.

The ligand 4C7NbF-CTV displays fluorescence at 450 nm (Fig. 2) because of the influence of 4-chloro-7-nitrobenzfuran in the CTV platform. An increase in the intensity of fluore-



Scheme-I: Synthetic route for the preparation of 4C7NbF-CTV

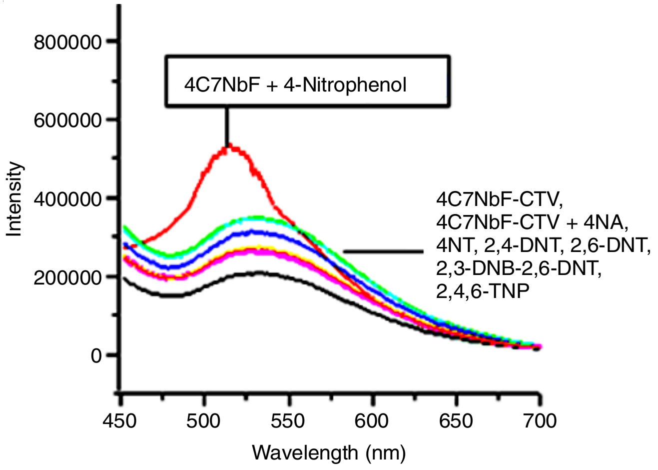


Fig. 2. Fluoroscence spectra of 4C7NbF-CTV with various nitro aromatic compounds

scence was noticed from 267109.353 cps to 453037.584 cps when 4-nitro phenol was added to 4C7NbF-CTV mixture and no change was observed on the addition of the rest of the nitro aromatic compounds.

The photo induced electron transfer (PET) mechanics can be used to explain the enhancement in the fluorescence intensity. PET binds an molecule with a fluorophore that changes the molecule binding and the recognition into a output signal that is fluoroscence [19]. Sensors on PET usually contains a receptor and a fluorophore that is separated by a short spacer electronically connecting the π-electron systems of both.

In 4C7NbF-CTV, the 4-chloro-7-nitrobenzfuran, has lone pair of electrons on oxygen atoms, when 4C7NbF-CTV binds with 4-nitro phenol, the mechanics of PET allows the increase in signalling in 4-nitro phenol (turn on). Due to the lone pair of electrons in the oxygen atoms of 4-chloro-7-nitrobenzfuran in the 4C7NbF-CTV platform, the mechanism of PET is followed which further leads to the increase (enhanced) fluorescence of 4C7NbF-CTV in presence of 4-nitrophenol.

As it can be seen in the Fig. 2 an increase in the intensity of 4C7NbF-CTV is been observed when bound with 4-nitrophenol from among the other nitroaromatic compounds. The newly developed molecule 4C7NbF-CTV is only liable for the detection of 4-nitrophenol. Further to reinforce the facts for the detection of 4-nitrophenol by 4C7NbF-CTV, parallel interference fluorescence studies were conducted, by taking the other nitroaromatic compounds with [4-nitrophenol + 4C7NbF-CTV] (Fig. 2). Further, from the emission study, we can say that 4C7NbF-CTV manifests enhancement for 4-nitrophenol with detection range between 50 μM to 1 mM (Fig. 3).

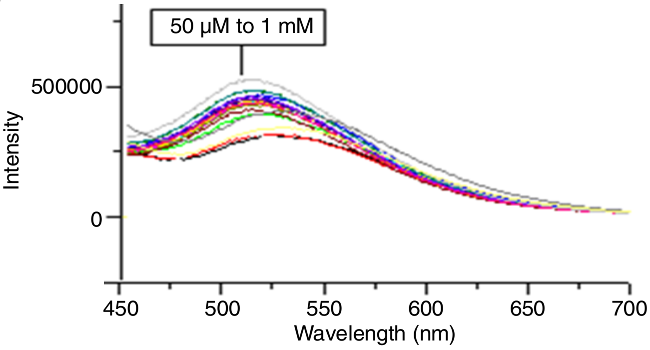


Fig. 3. Titration study 4C7NbF-CTV+4-nitrophenol

Studies of binding constant: In order to assess the binding constant for 4C7NbF-CTV, the increase in fluorescence intensity of 4-nitrophenol was carried out by fluorescence titration following the literature procedure [19-21]. A graph showing the changes observed in the intensities of fluorescence on adding increasing amount of concentration of ions is displayed in Figs. 2 and 3. Based on this procedure, the relationship of fluorescence intensity (F) to that of concentration of ion ([M]) is shown by the following equation:

$$\frac{(F_0 - F)}{(F - F_1)} = \left(\frac{[M]}{K_{diss}}\right)^n$$

on plotting a graph of log [(F_0-F)/(F-F_1)] *versus* log [M], binding constant (K_s) is obtained.

In the equation F_0 and F_1 denote the relative fluorescence intensities of the mixture without addition of recipient metal ion (guest) and with peak concentration of metal ion, respectively. The value of log (K_{diss}) is given by the value of log [M] at log [(F_0 – F)/(F – F_1)] = 0, the reciprocal of which is the binding constant (K_s).

The plots log [(F_0 – F)/(F – F_1)] *versus* log [M] for the given metal ions are shown as insets in (Fig. 4). The titration data shows an excellent linear fit (R = 0.909) from the equation.

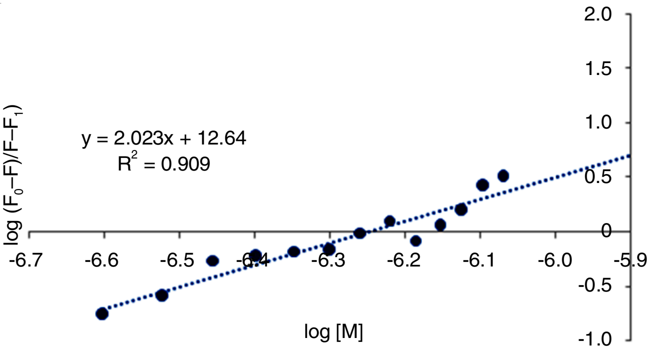


Fig. 4. Binding constant

The binding constants of the complex was found to be $0.002413 \times 10^4\ M^{-1}$ which demonstrates a strong binding of 4C7NbF-CTV and 4-nitro phenol.

Studies of quantum yield: The emission efficiency of the fluorophore attached to the CTV platform is denoted by quantum yield. Based on methods given in the literature [22,23] and the fluorescence studies of titration, using the following equation, the quantum yield was found out:

$$\Phi = \Phi_{sdt} \frac{(F \times A_{std} \times \eta)}{F_{std} \times A \times \eta_{std}}$$

where areas under the florescence emission curves of the 4-nitrophenol with 4C7NbF-CTV and the 4C7NbF-CTV are given by F and F_{std}, respectively. The relative absorbance of the sample and standard at the excitation wavelength are given by A and A_{std}. F represents the 4-nitrophenol complex with 4C7NbF-CTV and F_{std} represents the standard 4C7NbF-CTV.

η and η_{std} are the refractive indices of solvent (acetonitrile) used for the sample and standard, respectively, which both have the values 1.344. The quantum yield was found to be 0.92.

The chemical process approaches degradation n as the concentration of 4-nitrophenol increases, *i.e.*, increase in intensity (enhancement) happens.

Studies of Stern-Volmer analysis: To understand the mechanics of fluorescence enhancement, Stern-Volmer plots are useful [23,24] and therefore were used to study the features of the enhancement method in forming of the complex of 4-nitrophenol along with the ligand 4C7NbF-CTV. Based on the data, on plotting relative emission intensities (I_0/I) against quencher concentration [Q] dynamic or static quenching processes can be determined shown by the following equation, the slope of the line plotted gives K_{sv} which is known as the static quenching constant.

$$\frac{I_0}{I} = 1 + K_{sv}[Q]$$

A linearity of $R^2 = 0.995$ was observed. In present case, Fig. 5, presents the Stern-Volmer plots, a typical linear plot for 4-nitrophenol with 4C7NbF-CTV is shown indicating the process is simultaneously dynamic and static.

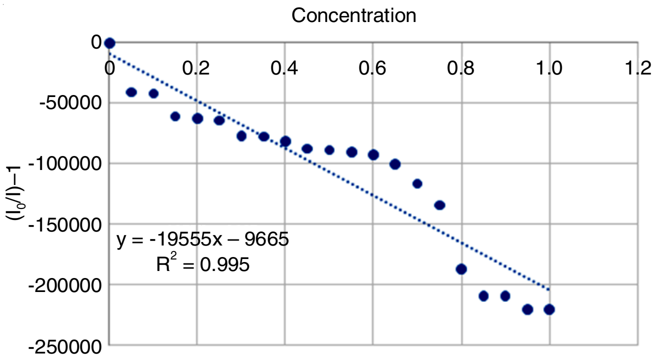


Fig. 5. Stern-Volmer analysis

Conclusion

To sum up, a new and novel sensor based on cyclotriveratrylene derivative has been developed and successfully (4C7NbF-CTV). (4C7NbF-CTV) behaves as a "turn-on" sensor for 4-nitro phenol among the various nitro compounds. Only 4-nitrophenol resulted in fluorescence enhancement. The studies proposes the mechanics for the enhancement in the fluorescence intensities. Furthermore studies based on the Binding constant analysis, quantum yield analysis and Stern-Volmer were successfully carried out which proposed a deeper insights in the mechanisms of the detection and binding of ligand and the guest molecule. Further research can be carried out in the detection of nitroaromatic phenols and effective sensors can be designed.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the various institutions for the help provided *viz.* Centre of Excellence COENFDD Centre, Rajkot, oxygen healthcare, Gujarat University for providing instrumental facilities and library facilities.

CONFLICT OF INTEREST

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

REFERENCES

1. L.G. Sultatos, *Toxicol. Appl. Pharmacol.*, **86**, 105 (1986); https://doi.org/10.1016/0041-008X(86)90403-5
2. L. Somasundaram, J.R. Coats and K.D. Racke, *J. Environ. Sci. Health B*, **24**, 457 (1989); https://doi.org/10.1080/03601238909372661
3. M.P. Carver, P.E. Levi and J.E. Riviere, *Pestic. Biochem. Physiol.*, **38**, 245 (1990); https://doi.org/10.1016/0048-3575(90)90096-K
4. W.A. House, D. Leach, J.L.A. Long, P. Cranwell, C. Smith, L. Bharwaj, A. Meharg, G. Ryland, D.O. Orr and J. Wright, *Sci. Total Environ.*, **194-195**, 357 (1997); https://doi.org/10.1016/S0048-9697(96)05375-2
5. M.D. Webber and C. Wang, *Can. J. Soil Sci.*, **75**, 513 (1995); https://doi.org/10.4141/cjss95-073
6. D.C. Trumbore, *Environ. Prog.*, **17**, 53 (1998); https://doi.org/10.1002/ep.670170120
7. N.A. Marley, J.S. Gaffney and M.M. Cunningham, *Environ. Sci. Technol.*, **27**, 2864 (1993); https://doi.org/10.1021/es00049a029
8. K. Levsen, S. Behnert, P. Mußmann, M. Raabe and B. Prieß, *Int. J. Environ. Anal. Chem.*, **52**, 87 (1993); https://doi.org/10.1080/03067319308042851
9. H.S. Rosenkranz and G. Klopman, *Mutagenesis*, **5**, 425 (1990); https://doi.org/10.1093/mutage/5.5.425
10. P. Fernandez, M. Grifoll, A.M. Solanas, J.M. Bayona and J. Albaiges, *Environ. Sci. Technol.*, **26**, 817 (1992); https://doi.org/10.1021/es00028a024
11. A. Niaz, J. Fischer, J. Barek, B. Yosypchuk, Sirajuddin and M.I. Bhanger, *Electroanalysis*, **21**, 1786 (2009); https://doi.org/10.1002/elan.200904622
12. P. Mulchandani, C.M. Hangarter, Y. Lei, W. Chen and A. Mulchandani, *Biosens. Bioelectron.*, **21**, 523 (2005); https://doi.org/10.1016/j.bios.2004.11.011
13. E.P.A. Method, *Fed. Regist.*, **26**, 58 (1984).
14. E.P.A. Method, *Fed. Regist.*, **26**, 153 (1984).
15. A. Niazi and A. Yazdanipour, *J. Hazard. Mater.*, **146**, 421 (2007); https://doi.org/10.1016/j.jhazmat.2007.03.063
16. J.A. Padilla-Sánchez, P. Plaza-Bolaños, R. Romero-González, A. Garrido-Frenich and J.L. Martínez Vidal, *J. Chromatogr. A*, **1217**, 5724 (2010); https://doi.org/10.1016/j.chroma.2010.07.004
17. D. Hofmann, F. Hartmann and H. Herrmann, *Anal. Bioanal. Chem.*, **391**, 161 (2008); https://doi.org/10.1007/s00216-008-1939-6
18. A. Chakrabarti, H.M. Chawla, G. Hundal and N. Pant, *Tetrahedron*, **61**, 12323 (2005); https://doi.org/10.1016/j.tet.2005.09.101
19. N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, **41**, 1130 (2012); https://doi.org/10.1039/C1CS15132K
20. K.D. Bhatt, B.A. Makwana, D.J. Vyas, D.R. Mishra and V.K. Jain, *J. Lumin.*, **146**, 450 (2014); https://doi.org/10.1016/j.jlumin.2013.10.004
21. S.M. Darjee, D.R. Mishra, K.D. Bhatt, D.J. Vyas, K.M. Modi and V.K. Jain, *Tetrahedron Lett.*, **55**, 7094 (2014); https://doi.org/10.1016/j.tetlet.2014.10.149
22. K.D. Bhatt, H.S. Gupte, B.A. Makwana, D.J. Vyas, D. Maity and V.K. Jain, *J. Fluoresc.*, **22**, 1493 (2012); https://doi.org/10.1007/s10895-012-1086-5
23. C.B. Murphy, Y. Zhang, T. Troxler, V. Ferry, J.J. Martin and W.E. Jones, *J. Phys. Chem. B*, **108**, 1537 (2004); https://doi.org/10.1021/jp0301406
24. S. Fery-Forgues and D. Lavabre, *J. Chem. Educ.*, **76**, 1260 (1999); https://doi.org/10.1021/ed076p1260