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Synthesis of 5,10,15,20-tetra[6′-nitro-1,3,3-trimethylspiro(indolino-2,2′-2*H*-chromen-5-yl)]porphyrin and its metal complexes

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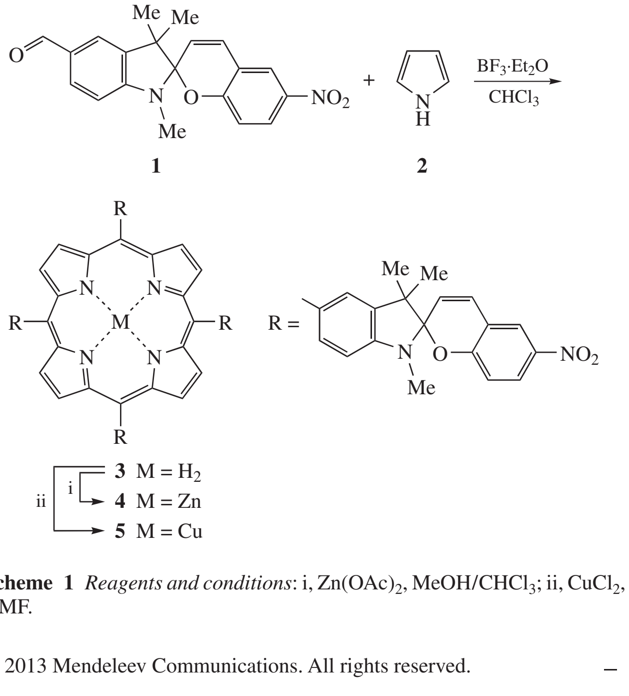
A new 5,10,15,20-tetrasubstituted porphyrin containing four 6′-nitro-1,3,3-trimethylspiro(indolino-2,2′-2*H*-chromene) substituents and its complexes with Zn^{2+} and Cu^{2+} ions were prepared and characterized by physicochemical methods of analysis.

The tetrapyrrole macroheterocyclic compounds of porphyrin type are of interest because of their important functions in living organisms (the prosthetic groups of the hemoproteins of hemoglobins, myoglobin and cytochromes; the constituents of chlorophyll, pheophytin, enzymes *etc*.) and a unique set of the physicochemical properties of their molecules.[1] Frequently, these molecules play the role of an antenna and/or conductor in living and artificial systems for the collection and transfer of light energy to reaction centres where the main photochemical reaction occurs.[2,3] The specific photosensitivity of porphyrins made it possible to develop medicinal preparations, catalysts, sensors and different materials for optics and electronics on their basis.[4] Synthetic methods for the preparation of porphyrins have been much studied, and the properties of these molecules can be regulated by varying substituents and their ability to form metal complexes.[5] The photochemical properties of porphyrins can be controlled (turned on or off) by modification with photochromic moieties.[2,6] Thus, a spiropyran molecule was covalently bound to porphyrin, or a mixture of these compounds in solution was used. However, in the former case, the effectiveness of photocontrol was not high, and the latter approach is inconvenient from the viewpoint of wide applications.



Scheme 1 *Reagents and conditions*: i, $Zn(OAc)_2$, $MeOH/CHCl_3$; ii, $CuCl_2$, DMF.

Here, we report the synthesis and spectroscopic characterization of a new porphyrin containing four photochromic molecules of 6′-nitrospiro(benzopyran) and its complexes with Zn^{2+} and Cu^{2+} ions (Scheme 1).

The target 5,10,15,20-tetra[6′-nitro-1,3,3-trimethylspiro(indolino-2,2′-2*H*-chromen-5-yl)]porphyrin **3** was synthesized according to Lindsey[7] with the separate steps of formation and subsequent oxidation of the porphyrinogen. At the first step, a mixture of 6′-nitro-1,3,3-trimethyl-5-formylspiro(indolino-2,2′-2*H*-chromene) **1**,[8] pyrrole **2** and a $BF_3{\cdot}Et_2O$ catalyst in chloroform was boiled in an atmosphere of argon. At the second step, oxidant *p*-chloranil was added, and the mixture was heated with stirring. The yield of product **3** was 27% after flash chromatography.

Then, complexation properties of porphyrin **3** were tested. Zinc complex **4** was prepared by heating compound **3** with zinc acetate in chloroform. In the course of reaction, colour changed to green. Copper complex **5** was obtained by heating compound **3** with $CuCl_2$ in DMF. Preliminary studies of their photochromic behaviour in chloroform solutions were performed.

Tetraphenylporphyrin (TPP) was used as a reference compound. Under irradiation at 254 nm mode we observed the disappearance of main absorption bands (Soret bands) at 436 and 418 nm for compound **3** and TPP, respectively, and the appearance of bands at 473 and 738 nm for **3**; 445 and 661 nm for TPP (see Online Supplementary Materials). Subsequent storage of samples in the dark did not cause principal changes.

We have considered a number of possible options for the processes: (i) degradation of one or more C=C bonds in the pyrrole ring of a porphyrin cycle with the production of chlorin/bacteriochlorin structures;[9] (ii) formation of the aggregated states;[10] and (iii) protonation of tetrapyrrole moiety.[11] TLC monitoring on both silica gel and alumina plates did not reveal difference between the chromatographic mobility and visualization of initial compound **3** and its irradiated form. In the ^1H NMR spectra of **3** after irradiation at 254 nm noticeable change for the signals was observed: β-H porphyrin protons – shift to strong field by 0.5 ppm and the disappearance of NH protons in the region –2.56 ppm (signal type and exact displacement could not be determined reliably because of the broadening of the signals and presence of the signals of photodegradation byproducts). Addition of trifluoroacetic acid (TFA) or hydrochloric acid to **3** and TPP led to the same effects as 254 nm radiation. Addition of triethylamine (TEA) to the irradiated solution of **3** returns the

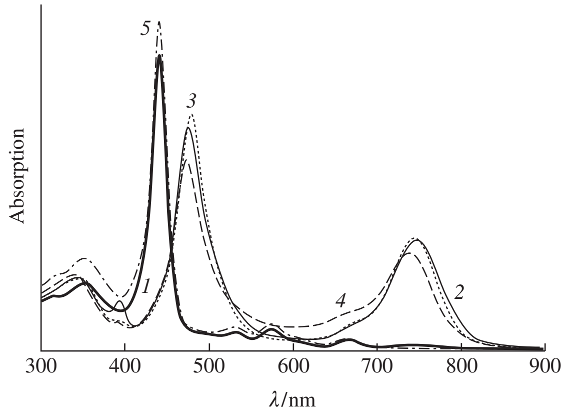


Figure 1 Absorption spectra of compound **3** (~10^{-5} M chloroform solution) at 25 °C: (*1*) initial solution, (*2*) after TFA addition, (*3*) after HCl addition, (*4*) upon UV-254 illumination and (*5*) upon the subsequent TEA addition.

absorption curves to the initial positions before irradiation (Figure 1). Most likely, under UV irradiation of chloroform solutions in the presence of oxygen the photodecomposition of solvent takes place and significant release of hydrogen chloride which protonated free tetrapyrrole fragments occurs.

Interestingly, upon the protonation of spiropyran-substituted porphyrin **3**, Q and the Soret bands undergo significant bathochromic shifts of 85 and 35 nm, respectively, and the ratio of absorption intensities of these bands became 0.5, whereas the values for TPP are 10:27:0.1. Similar to **3** results were obtained for the pyrrolemethanepyrrole-substituted porphyrin, 90:16:0.56, the pyrrole analogue under the same conditions showed a value of 47(dQ):0.21.[11(*a*)] The authors suggest that significant bathochromic shifts were caused by the interaction of nitrogen heterocycles with protonated pyrrole core porphyrin moieties.

Additional illumination at 254 nm or storage in the dark had no effect on the character and intensity of the absorption bands of TPP; however, it caused changes in the absorption spectra of compound **3**: a decrease in absorption intensity at 473 and 738 nm and an increase at 675 and 800 nm; the subsequent storage in the dark returned the system to the initial state (see Online Supplementary Materials). It is likely that the protonated form of **3**, obtained upon primary irradiation with light at 254 nm, retained its ability to the photocoloration of individual spiropyran units in the molecule.

The irradiation of solutions of compounds **3** and TPP at 365 nm resulted in consequences analogous to those with the use of light at 254 nm. For **3**: (i) increase in the intensity of absorption bands at 473 and 740 nm and a decrease at 436 nm were observed, moreover, this process occurred considerably slower than that under irradiation at 254 nm; (ii) increase in the absorption intensity at 555 (sh) and 600 nm with its subsequent restoration to the original values upon storage in the dark. The latter property corresponds to a photochromic transition of a spiro form into a merocyanine (MC) form, and it is thermally reverse for the spiropyran moiety of compound **3**.[12] For TPP: weak changes only at 418, 446 and 660 nm were detected (see Online Supplementary Materials). It appears that irradiation at 365 nm is more productive to photocoloration of spiropyran moiety and less efficient to generate HCl.

Upon protonation the metal complex **4** behaved similar to **3** [Figure 2(*a*)] and the transition to a new state for **5** (10 nm hypsochromic shift and decrease in absorption intensity of the Soret band) – curve *3* in Figure 3(*a*) (further addition of acid

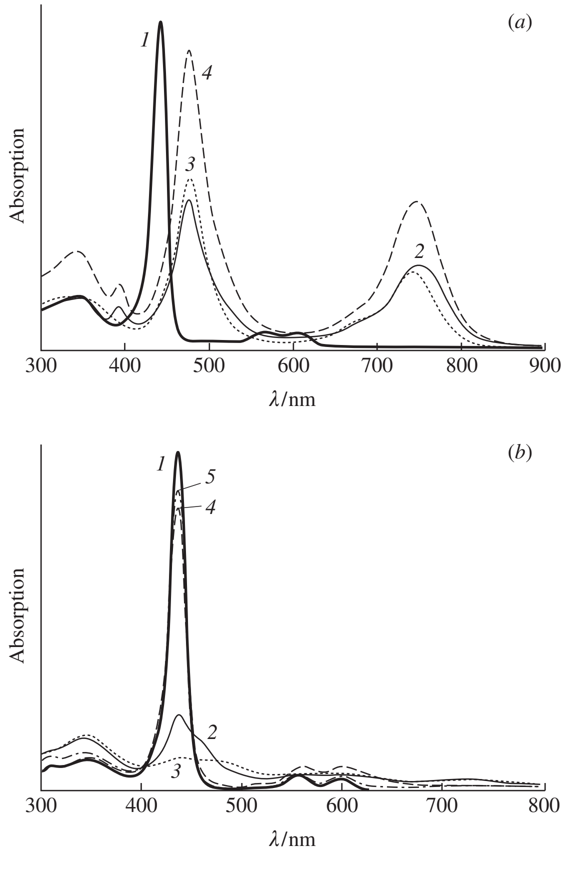


Figure 2 Absorption spectra in ~10^{-5} M chloroform solution at 25 °C. (*a*): (*1*) Initial solution of **4**, (*2*) after TFA addition, (*3*) after HCl addition, (*4*) solution of **3** after HCl addition; (*b*): (*1*) initial solution of **4**, (*2*) upon UV-254 illumination, (*3*) further UV-254 illumination, (*4*) upon UV-365 illumination, (*5*) subsequent keeping in the dark.

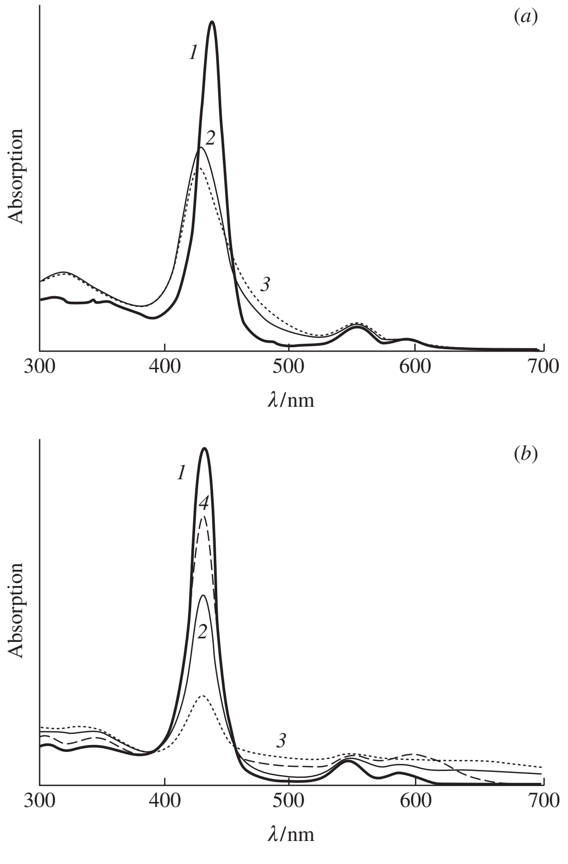


Figure 3 Absorption spectra in ~10^{-5} M chloroform solution at 25 °C. (*a*): (*1*) Initial solution of **5**, (*2*) after TFA/HCl addition, (*3*) subsequent TFA/HCl addition; (*b*): (*1*) initial solution, (*2*) upon UV-254 illumination, (*3*) further UV-254 illumination, (*4*) upon UV-365 illumination.

causes no change). Apparently, under acidification zinc is readily displaced from complex **4**, the copper complex, however, is resistant to such a treatment (presumably, some modifications are caused by aggregation).

In contrast to **3** or TPP, under illumination at 254 nm metal complexes **4** and **5** undergo rapid degradation (Figures 2 and 3), which was noticeably more rapid for **4** than for **5** [curves *2* and *3* in Figures 2(*b*) and 3(*b*)]. The irradiation at 365 nm of the solutions of **4** and **5** led to a decrease in absorption in the Soret region (430–440 nm) and an increase in three bands at 457, 570–580 and 610–620 nm, and after storage in the dark, the absorption curves of **4** and **5** returned to the initial positions. This behaviour of compounds **4** and **5** is also consistent with the photochromic transformations of spirobenzopyrans in solutions, where a band at 500–580 nm corresponds to the absorption of the MC form and a longer wave region of 580–650 nm corresponds to the aggregated state of MC (for aprotic solvents).[13]

Thus, we synthesized new photochromic porphyrins whose derivatives may be useful in catalytic, therapeutic or sensor systems and whose properties will be investigated in detail and reported elsewhere.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.07.006.

References

1 (*a*) *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, Amsterdam, 1975; (*b*) *Handbook of Porphyrin Science*, eds. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, River Edge, New York, 2013; (*c*) H. Brunner, H. Obermeier and R.-M. Szeimie, *Chem. Ber.*, 1995, **128**, 173; (*d*) M. G. Walter, A. B. Rudine and C. C. Wamser, *J. Porphyrins Phthalocyanines*, 2010, **14**, 759; (*e*) Y. Kuramochi, A. Satake and Y. Kobuke, *J. Am. Chem. Soc.*, 2004, **126**, 8668; (*f*) M. B. Winter, P. J. Klemm, C. M. Phillips-Piro, K. N. Raymond and M. A. Marletta, *Inorg. Chem.*, 2013, **52**, 2277; (*g*) M. Schliep, G. Cavigliasso, R. G. Quinnell, R. Stranger and A. W. Larkum, *Plant Cell Environ.*, 2013, **36**, 521; (*h*) X. F. Wang and O. Kitao, *Molecules*, 2012, **17**, 4484; (*i*) C. S. Lin, M. J. Lee, S. B. Park and M. C. Kiernan, *Clin Neurophysiol.*, 2011, **122**, 2336.

2 (*a*) T. B. Norsten and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 1784; (*b*) J. Frey, G. Kodis, S. D. Straight, T. A. Moore, A. L. Moore and D. Gust, *J. Phys. Chem. A*, 2013, **117**, 607; (*c*) S. D. Straight, G. Kodis, Y. Terazono, M. Hambourger, T. A. Moore, A. L. Moore and D. Gust, *Nat. Nanotechnol.*, 2008, **3**, 280.

3 (*a*) M. D. Ward, *Chem. Soc. Rev.*, 1997, **26**, 365; (*b*) J. S. Lindsey, D. F. Bocian and R. J. Donohoe, *J. Am. Chem. Soc.*, 1996, **118**, 11181; (*c*) S. Prathapan, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1993, **115**, 7519; (*d*) M. S. Vollmer, F. Wurther, F. Effenberger, P. Emele, D. U. Meyer, T. Stumpfig, H. Port and H. C. Wolf, *Chem. Eur. J.*, 1998, **4**, 260; (*e*) R. F. Kelley, S. J. Lee, T. M. Wilson, Y. Nakamura, D. M. Tiede, A. Osuka, J. T. Hupp and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2008, **130**, 4277.

4 (*a*) M. Ethirajan, P. Joshi and R. K. Pandey, *Chem. Soc. Rev.*, 2011, **40**, 340; (*b*) R. Bonnett, R. D. White and U.-J. Winifield, *Biochem. J.*, 1989, **261**, 277; (*c*) Y. Lv, M. Cao, J. Li and J. Wang, *Sensors (Basel)*, 2013, **13**, 3131; (*d*) D. Vlascici, E. Fagadar-Cosma, I. Popa, V. Chiriac and M. Gil-Agusti, *Sensors (Basel)*, 2012, **12**, 8193; (*e*) T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori and H. Naka, *J. Am. Chem. Soc.*, 2013, **135**, 50.

5 (*a*) *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, Boston, 2000, vol. 1; (*b*) M. O. Senge and J. Richter, *J. Porphyrins Phthalocyanines*, 2004, **8**, 934; (*c*) C. J. Medforth, M. D. Berber, K. M. Smith and J. A. Shelnutt, *Tetrahedron Lett.*, 1990, **31**, 3719; (*d*) M. G. H. Vicente, L. Jaquinod and K. M. Smith, *Chem. Commun.*, 1999, 1771; (*e*) F. Dumoulin and V. Ahsen, *J. Porphyrins Phthalocyanines*, 2011, **15**, 481; (*f*) I. S. Lonin, M. A. Grin, A. A. Lakhina and A. F. Mironov, *Mendeleev Commun.*, 2012, **22**, 157.

6 (*a*) J. L. Bahr, G. Kodis, L. Garza, S. Lin, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 2001, **123**, 7124; (*b*) Y. Liu, M. Fan, S. Zhang and J. Yao, *J. Phys. Org. Chem.*, 2007, **20**, 884.

7 (*a*) J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827; (*b*) J. S. Lindsey and R. W. Wagner, *J. Org. Chem.*, 1989, **54**, 828; (*c*) J. S. Lindsey, H. C. Hsu and I. C. Schreiman, *Tetrahedron Lett.*, 1986, **27**, 4969; (*d*) K. A. Formirovsky, N. A. Bragina, A. F. Mironov, G. A. Anan'eva, V. V. Bykova and N. V. Usol'tseva, *Mendeleev Commun.*, 2012, **22**, 278.

8 A. V. Laptev, A. Yu. Lukin, N. E. Belikov, V. I. Shvets, O. V. Demina, V. A. Barachevsky and A. A. Khodonov, *RF Patent, 2358977*, 2008 (*Chem. Abstr.*, 2009, **151**, 56831).

9 (*a*) A. F. Mironov and M. A. Grin, *J. Porphyrins Phthalocyanines*, 2008, **12**, 1163; (*b*) M. O. Senge, *J. Photochem. Photobiol. B*, 1992, **16**, 3; (*c*) M. V. Parkhats, V. A. Galievskii, E. S. Zharnikova, V. N. Knyukshto, S. V. Lepeshkevich, A. S. Stashevskii, B. M. Dzhagarov and T. V. Trukhacheva, *J. Appl. Spectrosc.*, 2011, **78**, 278; (*d*) P. M. Migensh, M. L. G. Arnaut, S. S. J. Formoziniu and K. Monteyro, *RF Patent, 2399622*, 2005; (*e*) A. Kozyrev, G. Zheng and C. Zhu, *Tetrahedron Lett.*, 1996, **37**, 6431.

10 (*a*) S. Biswas, H.-Y. Ahn, M. V. Bondar and K. D. Belfield, *Langmuir*, 2012, **28**, 1515; (*b*) S. Deng and R. C. Advincula, *Macromol. Rapid Commun.*, 2011, **32**, 1634; (*c*) K. Zelenka, T. Trnka, I. Tislerova, D. Monti, S. Cinti, M. L. Naitana, L. Schiaffino, M. Venanzi, G. Laguzzi, L. Luvidi, G. Mancini, Z. Novakova, O. Simak, Z. Wimmer and P. Drasar, *Chem. Eur. J.*, 2011, **17**, 13743; (*d*) C. Iacovita, P. Fesser, S. Vijayaraghavan, M. Enache, M. Stohr, F. Diederich and T. A. Jung, *Chem. Eur. J.*, 2012, **18**, 14610.

11 (*a*) H. Furuta, H. Maeda, T. Furuta and A. Osuka, *Org. Lett.*, 2000, **2**, 187; (*b*) L. R. Milgrom, J. P. Hill and P. J. F. Dempsey, *Tetrahedron*, 1994, **50**, 13477.

12 (*a*) *Photochromism. Molecules and Systems*, eds. H. Dürr and H. Bouas-Laurent, Elsevier, London, 2003; (*b*) *Organic Photochromic and Thermochromic Compounds*, eds. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999.

13 (*a*) V. A. Barachevskii and R. E. Karpov, *High Energy Chem.*, 2007, **41**, 188 (*Khim. Vys. Energ.*, 2007, **41**, 226); (*b*) *Aggregation Processes in Solution*, eds. E. Wyn-Jones and J. Gormally, Elsevier, Amsterdam, 1983, ch. 10–12; (*c*) P. Uznanski, *Synth. Met.*, 2000, **109**, 281.

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