Photophysical properties of the new phosphorescent platinum(II) and palladium(II) complexes of benzoporphyrins and chlorins

S.M. Borisov [a],[*], D.B. Papkovsky [b], G.V. Ponomarev [c], A.S. DeToma [d], R. Saf [e], I. Klimant [a]

[a] Institute of Analytical Chemistry and Radiochemistry, Graz University of Technology, Stremayrgasse 16, 8010 Graz, Austria
[b] Department of Biochemistry, University College Cork, Cavanagh Pharmacy Building, College Road, Cork, Ireland
[c] Institute of Biomedical Chemistry, Pogodinskaia St. 10, Moscow 119121, Russia
[d] Department of Chemistry and Biochemistry, Elizabethtown College, One Alpha Drive, Elizabethtown, PA 17022, United States
[e] Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 16, 8010 Graz, Austria

ARTICLE INFO

ABSTRACT

Several phosphorescent platinum(II) and palladium(II) complexes of tetrapyrrole dyes are prepared in an attempt to improve the compatibility with red laser diodes. The nature of *meso*-substituents in benzo-porphyrin macrocycle is found to affect mainly the position of the Soret band and has little influence on the Q-bands. In rigid polymeric matrices these dyes possess more favourable photochemical properties than corresponding *meso*-tetraphenyltetrabenzoporphyrins. Platinum(II) chlorins show good compatibility with 635 nm laser diode and 632.8 line of He–Ne laser, and have moderate brightness with emission yields ∼2%. Photophysical properties and photostability of these dyes is assessed and compared with the known NIR-emitting oxygen indicators.

1. Introduction

Oxygen is one of the most important analytes, it can be monitored routinely by electrochemical or optical means. The latter allows noninvasive sensing and imaging of oxygen, miniaturization, relative simplicity and low cost [1,2]. Common oxygen-sensitive indicator dyes include phosphorescent Pt(II) and Pd(II) complexes of porphyrins such as octaethylporphyrin (OEP) [3–6], 5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin (TFPP) [7–9], octaethylporphine-ketone (OEPK) [10–12], benzo-porphyrins [13–15], and fluorescent complexes of ruthenium(II), particularly with tris-4,7-diphenyl-1,10-phenanthroline (Ru-dpp) [16–19]. In recent years, longwave oxygen indicators became increasingly popular [12,14,15,20,21] also because they allow mea-surements in highly scattering and fluorescent media. Moreover, red-light excitable indicators are the materials of choice for implantable sensors [22,23]. The NIR-emitting phosphorescent dyes were also shown to be promising for applications in OLEDs [24] and solar collectors [25].

Thus, Pt(II) and Pd(II) benzoporphyrins, which can be excited at longer wavelengths [14,15,26] than corresponding complexes of

porphyrin-lactones [27] and porphyrin-ketones [10], were demon-strated to be viable oxygen indicators [22,23]. Both are excitable with LEDs; however, only the Pd(II) complexes are compatible with 635 nm laser diode and 632.8 nm He–Ne laser. Notably, laser exci-tation enables confocal microscopy imaging, and laser diodes are particularly attractive in combination with optical fibers. Gener-ally, Pt(II) complexes are better suited for oxygen sensing due to their higher brightness and shorter phosphorescence decay time, and they provide optimal sensitivity (0–100% air saturation) when embedded in common polymeric matrices [23]. These factors stim-ulate the development of new longwave, laser-compatible oxygen indicators. In this work we describe the synthesis and photophysical characterization of several new phosphorescent *meso*-substituted Pt(II) benzoporphyrins and metallochlorins excitable with red light.

2. Experimental

2.1. Materials

4-Biphenyl-carboxaldehyde and 4-(*N*,*N*-diethylamino)benza-ldehyde were from Aldrich (www.sigmaaldrich.com), fluorene-2-carboxaldehyde, Pd(II) chloride, Pt(II) chloride—from ABCR (www.abcr.de), poly(vinyl chloride) (PVC)—from Fluka (www.sigmaaldrich.com), polysterene (MW 250,000)—from Fisher Scientific (www.fishersci.com), poly(ethylene glycol terephtha-

* Corresponding author. Tel.: +43 316 873 4326; fax: +43 316 873 4329.
E-mail address: sergey.borisov@tugraz.at (S.M. Borisov).

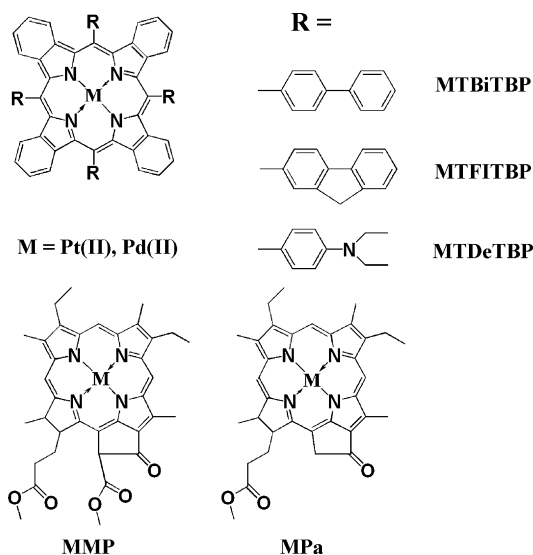**Fig. 1.** Chemical structures of the oxygen indicators.

late) support (Mylar®)—from Goodfellow (www.goodfellow.com). Pt(II) and Pd(II) complexes with OEP and TFPP were from Frontier Scientific (www.frontiersci.com), poly(octadecene-co-maleic anhydride) (PODMA)—from Scientific Polymer Products Inc. (www.scientificpolymer.com). Solvents were from Roth (www.carl-roth.de). Nitrogen and synthetic air (all of 99.999% purity) were from Air Liquide (www.airliquide.at).

PtOEPK and PdOEPK, and PdTFPP-lactone were synthesized as described in [10,27], respectively.

The palladium(II) complex with methylmesopheophorbide a (PdMMP, Fig. 1) was produced by heating solution of the ligand in dimethylformamide containing an excess of $PdCl_2$ for 10–15 min at 120–130 °C. The reaction mixture was then diluted with water. The formed precipitate was filtered, dried in air, redissolved in a minimum amount of methylene chloride, and purified by flash-chromatography on Silicagel G-60 (Merck) eluting with methylene chloride/ether (95:5). The main fraction was dried and recrystallized from methylene chloride/methanol. Yields were typically 75–85%. The platinum(II) complexes with MMP and methylmesopyropheophorbide a (MPa) were obtained by boiling the solutions of the ligands in propionic acid for 5–10 min in the presence of $PtCl_2(PhCN)_2$ with gradual addition of sodium acetate. Resulting PtMMP and PtMPa complexes were purified by chromatography as described above, and yields were 70–75%.

Palladium(II) methylmesopheophorbide a (PdMMP) MS (MALDI): m/z [M]$^+$ calc. 712.1877, found 712.19.

Platinum(II) methylmesopheophorbide a (PtMMP) MS (MALDI): m/z [M]$^+$ calc. 801.2490, found 801.26.

Platinum(II) methylmesopyropheophorbide a (PtMPa) MS (MALDI): m/z [M]$^+$ calc. 743.2435, found 743.40.

The platinum(II) and palladium(II) complexes of *meso*-substituted benzoporphyrins (Fig. 1) were prepared following the procedure reported previously [15] which includes preparation of reduced *meso*-substituted tetracyclohexeno-porphyrins, subsequent metallation and aromatization of the complexes. Corresponding 5,10,15,20-tetrakis-(biphenyl)-tetracyclohexenoporphyrin, 5,10,15,20-tetrakis-(fluoreno)tetra-cyclohexenoporphyrin and 5,10,15,20-tetrakis-(4-N,N-diethyl-laminophenyl)porphyrin were synthesized similar to the procedure [11], by condensation of 4,5,6,7-tetrahydroisoindole with 4-biphenyl-carboxaldehyde, fluorene-2-carboxaldehyde or 4-(N,N-diethylamino)benzaldehyde, respectively.

Platinum(II) 5,10,15,20-tetrakis-(biphenyl)tetrabenzoporphyrin (PtTBiTBP) MS (MALDI): m/z [M]$^+$ calc. 1310.3820, found 1310.3893.

Palladium(II) 5,10,15,20-tetrakis-(biphenyl)tetrabenzoporphyrin (PdTBiTBP) MS (MALDI): m/z [M]$^+$ calc. 1221.3251, found. 1221.3108.

Platinum(II) 5,10,15,20-tetrakis-(fluoreno)tetrabenzoporphyrin (PtTFlTBP) MS (MALDI): m/z [M]$^+$ calc. 1358.3820, found 1358.3881.

Palladium(II) 5,10,15,20-tetrakis-(fluoreno)tetrabenzoporphyrin (PdTFlTBP) MS (MALDI): m/z [M]$^+$ calc. 1268.3236, found 1268.3273.

Palladium(II) 5,10,15,20-tetrakis-(4-N,N-diethylaminophenyl) tetrabenzoporphyrin (PdTDeTBP) MS (MALDI): m/z [M]$^+$ calc. 1202.4939, found 1202.4961.

2.2. Preparation of polymer film coatings

The "cocktails" for coating were prepared by dissolving the indicator and the polymer (10%, w/w) in organic solvents. Chloroform was used for polystyrene and tetrahydrofuran was used for PVC and PODMA. The cocktails were knife coated on Mylar support to give, after solvent evaporation, phosphorescent sensor films, 2–6 μm thick. For PVC and PODMA the dye concentration in the polymer was 0.4–1% (w/w), and film thickness was adjusted to give an absorption value of ~0.15 at 405 nm. The polystyrene films contained ~0.5% (w/w) of the dye and had a thickness of 5 μm.

2.3. Measurements

Mass spectrometry was performed on a Micromass TofSpec 2E Time-of-Flight Mass Spectrometer. The instrument is equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz), and a time lag focusing unit. Ions were generated by irradiation just above the threshold laser power. Positive ion spectra were recorded in reflectron mode applying an accelerating voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethyleneglycol)s (PEG). The spectra of 100–150 shots were averaged to improve the signal-to-noise ratio. Analysis of data was done with MassLynx-Software V3.5 (Micromass/Waters, Manchester, UK). Samples were dissolved in THF ($C = 0.1$ mg mL^{-1}), dithranol was used as matrix ($C = 10$ mg mL^{-1} in THF). The solutions were mixed in the cap of a microtube in the ratio of 1 μL:10 μL. Then, 0.5 μL of the resulting mixture were deposited on the sample plate (stainless steel) and allowed to dry under air. Mass spectrometry for chlorins (PtMMP, PdMMP and PtMPa) was performed on Bruker Ultraflex II Mass Spectrometer. The instrument is equipped with Nd–YAG laser (20–100 Hz). Positive ion spectra were recorded in reflectron mode applying an accelerating voltage of 25 kV. Matrix—2,5-dihydroxybenzoic acid.

Absorption spectra in the range 300–800 nm were measured on a Cary 50 UV–vis spectrophotometer (www.lzs-concept.com). Emission spectra were acquired on a Hitachi F-7000 fluorescence spectrometer (www.inula.at) equipped with a red-sensitive photomultiplier R928 Hamamatsu (www.hamamatsu.com). Phosphorescence measurements at 77 K were performed in a homemade cryostat cooled with liquid nitrogen. Emission spectra were corrected for PMT sensitivity, which was calibrated with a halogen lamp.

Relative emission yields were determined as an average of the two independent measurements: (i) from the emission spectra recorded on the fluorescence spectrometer under the excitation at 405 or 600 nm using solutions of PtOEP in toluene ($\Phi = 0.415$ [28]) and PdTPTBP in toluene ($\Phi = 0.21$ [15]) as standards, respectively; (ii) from a lock-in amplifier (PreSens, www.presens.de) with silicon photodiode as photon counter, using 405-nm LED (www.roithner-laser.com) excitation and PtOEP as a standard, or using 425 and 624-nm LEDs and PdTPTBP as a standard. BG 12 excitation filter (Schott, www.schott.com) and OG 590 emission filter (Schott) were

used with both LEDs. The light of a 624-nm LED was filtered through a NIR-blocking Calflex X™ filter (Linos Photonics, www.linos.com), and an RG 9 (Schott) filter was used for the emission.

Phosphorescence decay times for the dyes in organic solvents and in polymer films were measured with a two-phase lock-in amplifier (SR830, Stanford Research Inc., www.thinksrs.com), exciting with a 435-nm LED (www.roithner-laser.com) and a BG-12 filter. The light was sinusoidally modulated at a frequency of 5000 or 700 Hz for the Pt(II) and Pd(II) complexes, respectively. Bifurcated fiber bundle guided the excitation light to the cuvette and emission back to a H5701-02 photomultiplier tube (Hamamatsu) through the RG 9 filter. Temperature was controlled by a cryostat ThermoHaake DC50. Gas mixtures for calibration were obtained using a gas mixing device (MKS, www.mksinst.com).

Photostability of the dyes was determined using a lock-in amplifier from PreSens. Sensor foils were positioned at 45° relative to the photodiode and the light source. Continuous irradiation was performed with unmodulated 405 nm LED (1 W, 300 mA, Roithner), and a 405 nm LED modulated at 916 Hz was used for interrogation, together with BG 12 excitation and RG 630 emission filters. The bleaching rates were corrected for the amount of the absorbed light at 405 nm.

3. Results and discussion

3.1. Absorption

Fig. 2a and b shows that absorption spectra of the Pt(II) and Pd(II) complexes of TFlTBP, TBiTBP and TPTBP are similar. Substitution of the *meso*-phenyl rings with biphenyl and fluorene results in bathochromic shifts due to increased conjugation. The Soret band shifts by 4 nm for biphenyl and by 7 nm for fluorene. The substitution affects the position of the Q-band to a smaller degree (~2 nm for both substituents). Although compatibility of both Pt(II) and
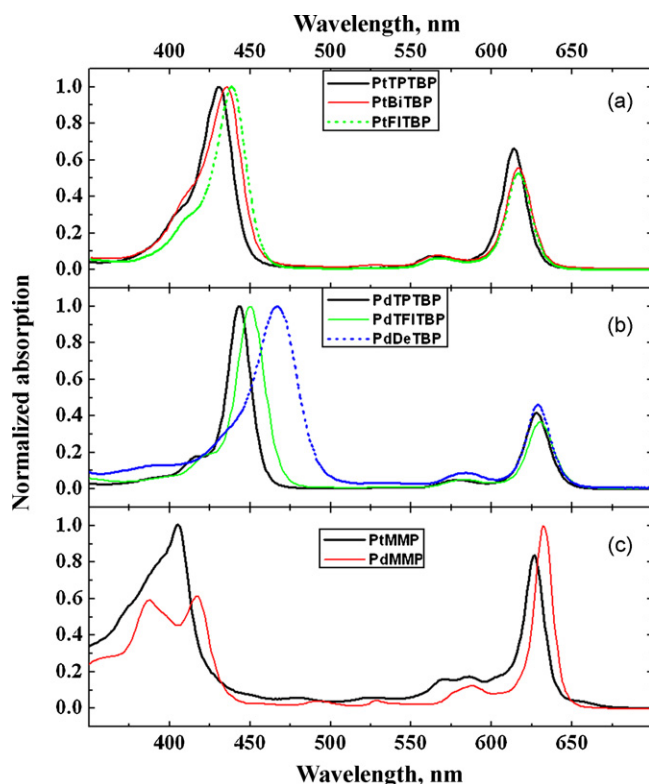
Pd(II) complexes with blue 450 nm LED excitation is improved considerably, compatibility of the Pt(II) complexes with 632.8 nm line of He–Ne laser and 635 nm laser diode is not good.

A pronounced (~20 nm) bathochromic shift of both the Soret band and the Q-bands for the Zn(II) complex of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin, relative to the Zn(II) complex with tetraphenylporphyrin, was reported [29]. We examined the influence of the *meso*-positioned electron-donating 4-diethylaminophenyl group on the spectral properties of benzoporphyrin complexes. PdTDeTBP, which could only be isolated with a very low yield, showed a bathochromic shift of the Soret band by ~25 nm relative to PdTPTBP (Fig. 2b, Table 1). The Soret band also becomes significantly brighter. However, the substitution has a low influence on the position of the first Q-band (~5 nm bathochromic shift) and the second Q-band at 629 nm is not affected by substitution.

PdTDeTBP was found to show acid–base equilibrium (Fig. 3). Protonation of the diethylamino group induces a pronounced hypsochromic shift of the Soret band (from 477 to 441 nm in DMF) while the Q-bands are virtually not affected. Notably, the Soret band of the protonated form becomes narrower and more intense.

Absorption spectra of Pt(II) and Pd(II) complexes of chlorins are shown in Fig. 2c. These dyes possess intense, narrow bands (half-width ~13 nm) in the red part of the spectrum, which are suitable for the excitation with both He–Ne laser and 635 nm laser diode.

3.2. Emission

Emission spectra in Fig. 4 show that all the dyes possess room temperature phosphorescence in the NIR region. The Pd(II) complexes emit at ~30 nm longer wavelengths than corresponding Pt(II) complexes. Substitution of the phenyl rings in *meso* positions of benzoporphyrin macrocycle with fluorene and biphenyl has only minor effect on the spectra. Pt(II) and Pd(II) complexes of chlorins emit at significantly longer wavelengths than benzoporphyrins.

Table 1 summarizes the photophysical properties of these oxygen indicators and compares them to parent Pt(II) and Pd(II) complexes of TPTBP, porphyrin-ketones and *meso*-substituted porphyrin-lactones. Interestingly, in oxygen-free solutions at room temperature both Pt(II) and Pd(II) complexes of TFlTBP and TBiTBP are weaker emitters that the respective complexes with TPTBP. Phosphorescence decay times of the complexes of TFlTBP and TBiTBP are ~2 times shorter and phosphorescence quantum yields
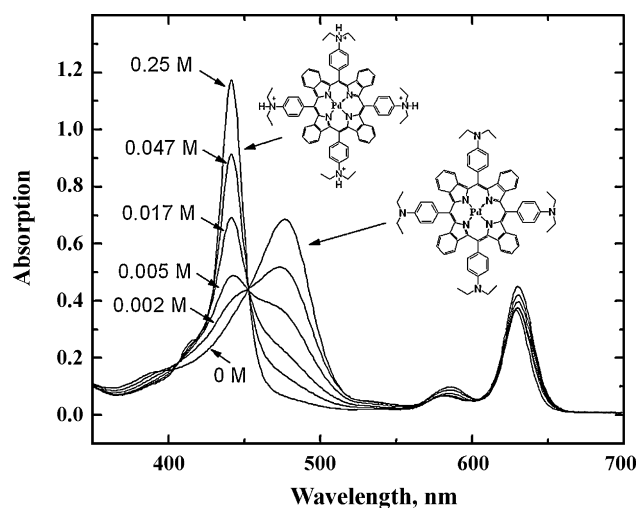

Fig. 2. Absorption spectra of the metal complexes of benzoporphyrins (a and b) and chlorins (c) in toluene.

Fig. 3. Absorption spectra of the PdTDeTBP in DMF (5×10^{-6} M solution) at varying concentration of the methansulfonic acid. DMF was chosen since it is a good solvent for both neutral and protonated form of the dye.

Table 1
Photophysical properties of red-light excitable oxygen indicators.

Dye	λ_{max} abs ($\varepsilon \times 10^{-3}$), nm ($M^{-1}$ cm^{-1})	λ_{max} em (nm)	Q.Y.	τ (μs)	λ_{max} em (77 K) (nm)	τ (77 K) (μs)	ET[a] (cm^{-1})	τ in PS (μs)	Relative Q.Y. in PS[b]
PtTPTBP	430 (205); 564 (16); 614 (136)	770	0.51	47	760	59	13,560	55	1.6
PtTFlTBP	437 (310); 567 (20); 616 (167)	772	0.30	25	761	60	13,140	52	2.3
PtTBiTBP	434 (178); 565 (14); 616 (99)	775	0.26	27	767	60	13,040	51	2.1
PtMMP	404 (1.00)[c], 572 (0.16), 583 (0.17), 625 (077)	820	0.02	8.4	813	13	12,300	12	∼0.05
PtMPa	403 (1.00), 573 (0.18), 625 (0.86)	819	0.02	9.0	814	–	12,290	12	∼0.05
PtOEPK	398 (88.2); 592 (55.1)[d]	761	0.21	63	755	84	13,250	59	0.8
PdTPTBP	443 (416); 578 (21); 628 (173)	800	0.21	286	792	430	12,630	370	1
PdTFlTBP	450 (280); 583 (17); 630 (105)	804	0.11	135	790	510	12,660	360	1.2
PdTBiTBP	447 (1.00)[c]; 582 (0.05); 630 (0.38)	805	0.11	155	791	490	12,640	360	1.1
PdTDeTBP	467 (155); 583 (14); 629 (71)	797	0.02	26	788	470	12,690	290	0.7
PdOEPK	410 (82.6); 603 (53.5)[d]	792	0.07	460	783	520	12,770	450	0.3
PdTFPPL	412 (120); 544 (9.4); 584 (39.2)[e]	768	0.09	520	759	570	13,180	410	0.2
PdMMP	387 (48.6); 417 (45.0); 586 (9.5); 633 (75.7)	849	0.01	61	848	–	11,790	–	<0.05

[a] Calculated from the emission spectra at 77 K.
[b] Q.Y. for PdTPTBP in PS is set as 1.
[c] Relative intensities.
[d] Ref. [10].
[e] Ref. [27].

∼2 times lower than for TPTBP. It is likely that the more bulky fluorene and biphenyl moieties interact with solvent molecules thus favouring non-radiative deactivation. However, in a rigid glass at 77 K, phosphorescence lifetimes of the complexes of TPTBP, TFlTBP and TBiTBP are all similar. When embedded in the polymers, phosphorescence yields increase significantly. Thus, Pt(II) and Pd(II) complexes of TFlTBP and TBiTBP in polystyrene possess emission yields higher than corresponding complexes of TPTBP (Table 1). Complexes of all three porphyrins show similar decay times in polystyrene.

Compared to PdTFlTBP and PdTBiTBP, phosphorescence of PdTDeTBP is even more strongly quenched in solution. Phosphorescence quantum yield is ∼10-fold lower and decay time is 10-fold shorter than for PdTPTBP. Such a strong quenching is most likely

to be caused by photoinduced electron transfer (PET) from diethylamino group to the macrocycle. This is confirmed by the fact that the protonated form of the dye (where no PET is possible) was found to be a much stronger emitter. In fact, in deoxygenated DMF the relative luminescence quantum yield improves ∼12-fold upon protonation, and the decay time increases from 9.8 to 113 μs. Again, the brightness and decay times increase at 77 K and in rigid PS, but not to the levels of PdTPTBP. It can be concluded that in solutions all the Pd(II) benzoporphyrins possess similar radiative constants k_r = Q.Y./τ (∼800 s^{-1}), but different non-radiative constants, k_{nr} = (1 − Q.Y.)/τ: PdTPTBP < PdTFlTBP $\cong$ PdTBiTBP < PdTDeTBP. On the other side, in rigid matrices such as PS the non-radiative constants are rather similar for all the Pd(II) complexes. The trend is similar for the Pt(II) benzoporphyrins.

Pt(II) and Pd(II) chlorin complexes are seen as much weaker emitters than corresponding benzoporphyrins, both in solution and in polystyrene. In agreement with the general trend, the yields for the Pt(II) chlorins are ∼2-fold higher than for the Pd(II) complexes. For the former they are estimated as ∼2% in solution.

Comparison of the photophysical properties of the new indicators shows that in solution and especially in polystyrene the complexes of benzoporphyrins possess higher quantum yields than porphyrin-ketones and meso-porphyrin-lactones (Table 1). Moreover, the former are excitable at longer wavelengths (both in the violet-blue and in the red part of the spectrum), and possess higher molar absorption coefficients ε. Their brightnesses (BS = ε Q.Y.) is therefore significantly higher.

3.3. Photostability

This property is of particular concern when optical measurements are performed over a prolong period of time or at high illumination intensities. Fig. 5 shows photodegradation profiles of different oxygen indicators. Poly(octadecene-co-maleic anhydride) is chosen for the Pt(II) complexes since it favours fast, easily measurable photodegradation, whereas in polystyrene the dyes are much more photostable and require longer irradiation times or higher light intensities. Photobleaching of the Pd(II) complexes was studied in PVC matrix which is less oxygen-permeable and which retains sufficient emission signals in aerated conditions. It was found that photostability of the complexes of TFlTBP, TBiTBP and TPTBP is rather similar. The benzoporphyrins degrade much faster than the porphyrin complexes (PtTFPP is known for its excellent photostability [30,31]). In poly(octadecene-co-maleic anhydride)
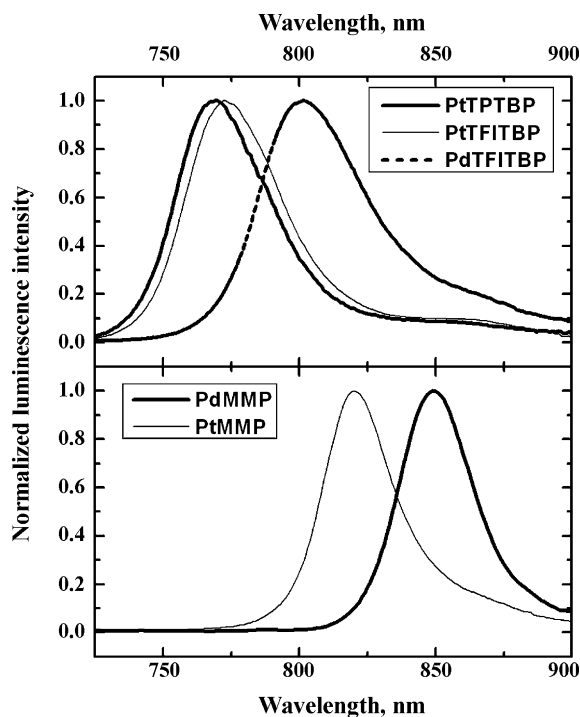
Fig. 4. Emission spectra of the oxygen indicators in deoxygenated toluene at RT (λ_{exc} was 405 nm for the benzoporphyrin complexes and 630 nm for the chlorin complexes).
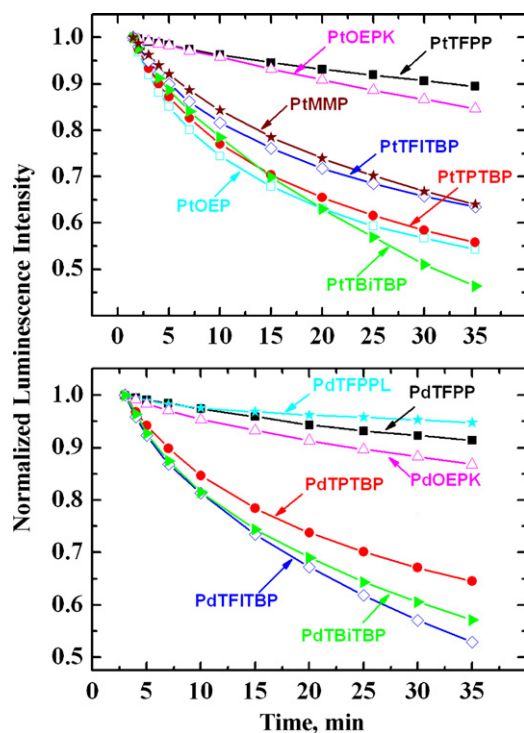
Fig. 5. Photodegradation of the oxygen indicators embedded in poly(octadecene-co-maleic anhydride), upper panel, and in poly(vinyl chloride), lower panel. The experiment was performed with the air-equilibrated foils at 25 °C using a 405-nm 1 W LED.

Fig. 6. Stern–Volmer plots for the Pt(II) and Pd(II) complexes embedded in polystyrene (at 25 °C). Curve fitting is performed according to Eq. (1).

benzoporphyrins photodegrade as quickly as PtOEP which has low photostability. Notably, in PS and PVC PtTPTBP showed a higher photostability than PtOEP [15,23]. Considering other indicators excitable with red light, photostability of the PdTFPPL is even better than that of PdTFPP. Pt(II) and Pd(II) complexes with OEPK are more photostable that the respective benzoporphyrins; however, they are less photostable than PtTFPP and PdTFPP. It should be noted that for sensing applications brightness of the indicators should also be considered. If two indicators have similar photobleaching rates but different brightness, the indicator with higher quantum yield will require lower excitation intensity (and therefore will bleach slower) to achieve the same signal as the indicator with low brightness. For example, complexes of porphyrin-ketones require significantly higher excitation intensities than the respective benzoporphyrins because of their moderate brightness (Table 1) and, therefore, will bleach approximately as fast as benzoporphyrins.

3.4. Oxygen sensing

Stern–Volmer plots for the indicators immobilized in polystyrene are shown in Fig. 6. Significant degree of non-linearity is observed, which is common for most oxygen-sensitive materials, including benzoporphyrins in PS [23]. The plots can be fitted using the "two-site model" [32], which assumes localization of an indicator in two different environments:

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \frac{f}{1 + K_{SV}[O_2]} + 1 - f, \tag{1}$$

where f and K_{SV} are fraction of the total emission and the Stern–Volmer constant for the first site, respectively (for the second site Stern–Volmer constant is assumed to be zero). As can be seen, the complexes of TBiTBP are quenched slightly more than the complexes of TFlTBP, K_{SV} values being 0.207, 0.183, 1.16 and 1.11 kPa^{-1} for PtTBiTBP, PtTFlTBP, PdTBiTBP and PdTFlTBP, respectively ($f = 0.89$ for all the complexes). The sensitivity of optodes based on these
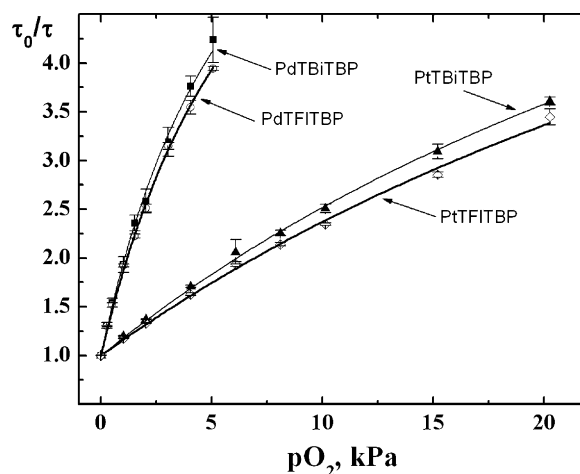
indicators is similar to that of the corresponding Pt(II) and Pd(II) complexes of TPTBP.

4. Conclusions

We have demonstrated that the new Pt(II) and Pd(II) complexes of TBiTBP and TFlTBP possess superior photophysical properties compared to the derivatives of TPTBP. Bathochromic shift of the Soret band (particularly for TFlTBP) significantly improves their compatibility with blue 450-nm LED. These dyes also possess higher emission quantum yields when embedded in polymers. These properties make them attractive for use in optical sensing. Pt(II) and Pd(II) complexes of the chlorins show good compatibility with 632.8 nm line of He–Ne laser and 635 nm laser diode. However, they exhibit modest emission yields both in solutions and in polystyrene which may limit their applicability.

References

[1] O.S. Wolfbeis, J. Mater. Chem. 15 (2005) 2657–2669.
[2] C. McDonagh, C.S. Burke, B.D. MacCraith, Chem. Rev. 108 (2008) 400–422.
[3] K. Eaton, B. Douglas, P. Douglas, Sens. Actuators, B 97 (2004) 2–12.
[4] B.-H. Han, I. Manners, M.A. Winnik, Chem. Mater. 17 (2005) 3160–3171.
[5] S.H. Im, G.E. Khalil, J. Callis, B.H. Ahn, M. Gouterman, Y. Xia, Talanta 67 (2005) 492–497.
[6] Y. Amao, I. Okura, H. Shinohara, H. Nishide, Polym. J. 34 (2002) 411–417.
[7] S. Grenoble, M. Gouterman, G. Khalil, J. Callis, L. Dalton, J. Lumin. 113 (2005) 33–44.
[8] M.E. Koese, B.F. Carroll, K.S. Schanze, Langmuir 21 (2005) 9121–9129.
[9] M.I.J. Stich, S. Nagl, O.S. Wolfbeis, U. Henne, M. Schaeferling, Adv. Funct. Mater. 18 (2008) 13991–21406.
[10] D.B. Papkovsky, G.V. Ponomarev, W. Trettnak, P. OïLeary, Anal. Chem. 67 (1995) 4112–4117.
[11] C. O'Donovan, J. Hynes, D. Yashunski, D.B. Papkovsky, J. Mater. Chem. 15 (2005) 2946–2951.
[12] E.J. Park, K.R. Reid, W. Tang, R.T. Kennedy, R. Kopelman, J. Mater. Chem. 15 (2005) 2913–2919.
[13] S.A. Vinogradov, D.F. Wilson, J. Chem. Soc. Perkin Trans. 2 (1995) 103–111.
[14] O.S. Finikova, A.V. Cheprakov, S.A. Vinogradov, J. Org. Chem. 70 (2005) 9562–9572.
[15] S.M. Borisov, G. Nuss, W. Haas, R. Saf, M. Schmuck, I. Klimant, J. Photochem. Photobiol. A: Chem. 201 (2009) 128–135.
[16] I. Klimant, O.S. Wolfbeis, Anal. Chem. 67 (1995) 3160–3166.
[17] Y. Amao, Microchim. Acta 143 (2003) 1–12.
[18] J. Hradil, C. Davis, K. Mongey, C. McDonagh, B.D. MacCraith, Meas. Sci. Technol. 13 (2002) 1552–1557.

[19] P. Roche, R. Al-Jowder, R. Narayanaswamy, J. Young, P. Scully, Anal. Bioanal. Chem. 386 (2006) 1245–1257.
[20] M. Gouterman, J. Callis, L. Dalton, G. Khalil, Y. Mebarki, K.R. Cooper, M. Grenier, Meas. Sci. Technol. 15 (2004) 1986–1994.
[21] B. Zelelow, G.E. Khalil, G. Phelan, B. Carlson, M. Gouterman, J.B. Callis, L.R. Dalton, Sens. Actuators, B 96 (2003) 304–314.
[22] I. Dunphy, S.A. Vinogradov, D.F. Wilson, Anal. Biochem. 310 (2002) 191–198.
[23] S.M. Borisov, G. Nuss, I. Klimant, Anal. Chem. 80 (2008) 9435–9442.
[24] C. Borek, K. Hanson, P.I. Djurovich, M.E. Thompson, K. Aznavour, R. Bau, Y. Sun, S.R. Forrest, J. Brooks, L. Michalski, J. Brown, Angew. Chem. Int. Ed. 46 (2007) 1109–1112.
[25] M.J. Currie, J.K. Mapel, T.D. Heidel, S. Goffri, M.A. Baldo, Science 321 (2008) 226–228.
[26] O.S. Finikova, A.V. Cheprakov, I.P. Beletskaya, P.J. Carroll, S.A. Vinogradov, J. Org. Chem. 69 (2004) 522–535.
[27] G. Khalil, M. Gouterman, S. Ching, C. Costin, L. Coyle, S. Gouin, E. Green, M. Sadilek, R. Wan, J. Yearyean, B. Zelelow, J. Porphyrins Phthalocyanines 6 (2002) 135–145.
[28] A.K. Bansal, W. Holzer, A. Penzkofer, T. Tsuboi, Chem. Phys. 330 (2006) 118–129.
[29] C.-W. Huang, K.Y. Chiu, S.-H. Cheng, Dalton Trans. (2005) 2417–2422.
[30] S. Lee, I. Okura, Anal. Commun. 34 (1997) 185–188.
[31] S.-W. Lai, Y.-J. Hou, C.-M. Che, H.-L. Pang, K.-Y. Wong, C.K. Chang, N. Zhu, Inorg. Chem. 43 (2004) 3724–3732.
[32] L. Sacksteder, J.N. Demas, B.A. DeGraff, J.R. Bacon, Anal. Chem. 65 (1993) 3480–3483.