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New Porphyrazine Macrocycles with High Viscosity-Sensitive Fluorescence Parameters

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Abstract—New tetraaryltetracyanoporphyrazines have been obtained in the form of metal complexes and free bases via template assembly of a variety of aryltricyanoethylenes as structural units of the macrocycle, and photophysical properties of the products have been studied. The unique high sensitivity of the fluorescent properties to viscosity has been demonstrated. This property opens the possibility of application of the said compounds as sensors of local viscosity. The prepared macrocycles exhibit significant photocytotoxicity, and can be thus used as sensitizers of photodynamic therapy.

Keywords: porphyrazine, fluorescence, photodynamic therapy, viscosity, molecular rotor

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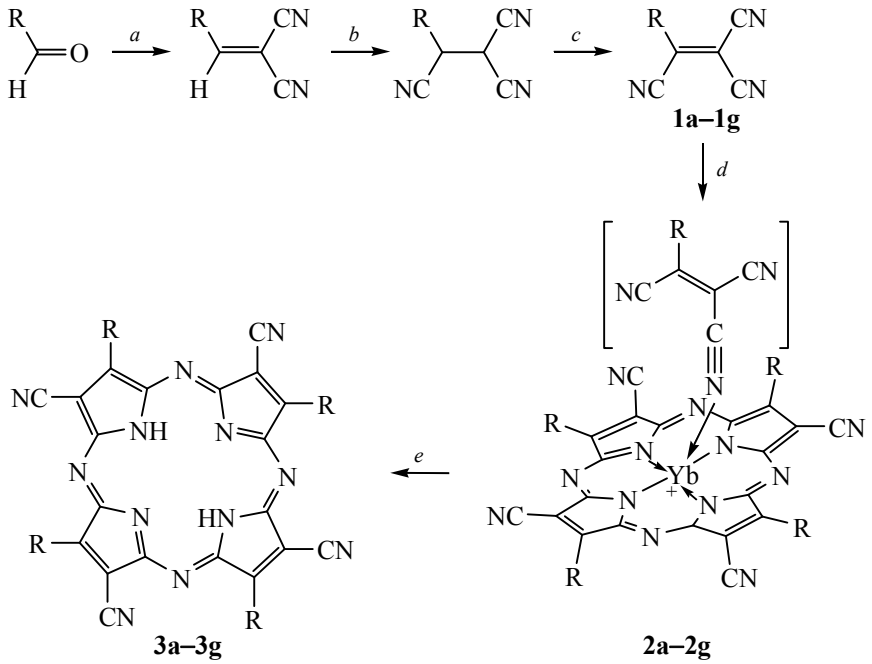
It was recently demonstrated that the fluorescent dyes of the porphyrazines class were promising agents for photodynamic therapy, since they could be selectively accumulated in the tumor tissue [1]. The photodynamic therapy is a popular optical method of treatment of various cancer types based on the photoinduced generation of unstable cytotoxic species like singlet oxygen by special dyes (photosensitizers) accumulated in a tumor [2].

We have earlier suggested a new approach to a template synthesis of porphyrazine dyes and have prepared for the first time the octacyanoporphyrazine macrocycle in the form of ytterbium or vanadyl complex [3]. The said method utilized the reaction of tetracyanoethylene with the corresponding sandwich metal complexes. It has been found that the interaction occurs at room temperature and the yield of the macrocyclic is unusually high for the template synthesis of porphyrazines. We have further extended the synthetic capacity of the approach by utilizing the template assembly of a series of aromatic tricyanoethylene derivatives. It has been demonstrated that the introduction of peripheral phenyl groups in the macrocycle results in a significant change in its spectral and electrochemical properties [4].

This work was aimed at a synthesis of a series of new tetraaryltetracyanoporphyrazines (in the form of free bases as well as metal complexes) via template assembly of various aryltricyanoethylenes and to study photophysical properties of the products. The high sensitivity of fluorescence parameters of the prepared porphyrazines to the medium viscosity resulted in a unique combination of properties of sensitizer of photodynamic therapy and optical sensor of local viscosity. It is important to notice that viscosity is an important parameter determining the rate of diffusion (and, hence, that of the bimolecular reactions) in the condensed phase. A change in the local viscosity in the biological systems can cause serious diseases and cells dysfunction or death. Therefore, the preparation of compounds acting as highly sensitive and non-invasive optical sensors of intracellular viscosity is a topical issue. On top of that, the compounds described in this paper are promising as potential sensitizers of photodynamic therapy. The high sensitivity of their fluorescence parameters to viscosity is an additional

Scheme 1.



a, $CH_2(CN)_2$, EtOH, 24 h, 20°C; *b*, KCN, H_2O, EtOH, 45 min, 20°C, then HCl; *c*, *N*-chlorosuccinimide, Et_2O; *d*, bis-indenylitterbium, THF, 24 h, vacuum; *e*, CF_3COOH, 30 min, 20°C. R = Ph (**a**), 4-FC_6H_4 (**b**), C_6F_5 (**c**), 2-naphthyl (**d**), 4-biphenyl (**e**), 2-tolyl (**f**), 2,6-xylenyl (**g**).

advantage opening the way to development of new technique of optical theranostics (a combination of therapy and diagnostics) of oncological diseases, based on the monitoring of intracellular viscosity in the course of photodynamic therapy.

The general scheme of preparation of porphyrazines **3a–3g** comprised the stages of aryltricyanoethylene synthesis [5], template assembly of the macrocycle at the Yb^{3+} cation, and elimination of the central cation to form the free base. The template assembly of tetracyanoethylene and 2-phenyl-1,1,2-tricyanoethylene into tetrapyrrole structure we have accomplished for the first time using sandwich bis-indenyl π-complex of ytterbium(II) [3, 4] (Scheme 1).

Utilization of various aromatic derivatives of tricyanoethylene as precursors in the template synthesis of the macrocycles can be regarded as a way to chemical design of periphery of the porphyrazines. The Structure of the tricyanoethylene derivatives **1a–1g** was confirmed by X-ray diffraction data (Fig. 1 and Table 1).

Compounds **2a–2g** possessed typical electron absorption spectra of porphyrazine complexes containing the Soret and *Q* bands (Fig. 2). The corresponding molar absorptivities were fairly high (log ε ~ 4), typical of the porphyrazine dyes as well. It is interesting to note that the substitution of hydrogen atoms in the phenyl rings with fluorine or bulky aryl substituents (**2d**, **2e**) resulted in the red shift of the *Q* band.

The presence of the axial fragment in the complexes **2a–2g** was confirmed by IR spectroscopy data (Table 2). IR spectra of the prepared compounds contained two absorption bands assigned to the C≡N bond vibrations. The first one, at higher frequency, was assigned to peripheral cyano groups of the macrocycle, in view of the data for the earlier described ytterbium tetraphenyltetracyanoporphyrazinate [4]. The second band corresponding to the lower bond energy is typical of anionic forms of aromatic tricyanoethylene derivatives (Table 2) [6]. It should be noted that the absorption bands of C≡N groups of the starting aryltricyanoethylenes were not observed in the spectra of the metal complexes **2a–2g**.

Macrocyclic structure of the complexes **2a–2g** was further confirmed by the presence of the bands characteristic of skeletal vibrations of the macrocycle ($\nu_{C=C}$) and pyrrole rings ($\nu_{C=N}$) in the IR spectra.

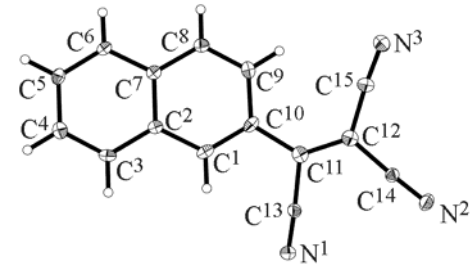
Table 1. Basic crystallographic data and parameters of diffraction experiment and structure refinement of compounds **1b** and **1d–g**

Parameter	Value				
	1b	**1d**	**1e**	**1f**	**1g**
Elemental formula	$C_{11}H_4FN_3$	$C_{15}H_7N_3$	$C_{17}H_9N_3$	$C_{12}H_7N_3$	$C_{13}H_9N_3$
Molar mass	197.17	229.24	255.27	193.21	207.23
Temperature, K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Rhombic	Monoclinic	Monoclinic	Rhombic	Rhombic
Space group	*Pccn*	$P2_1/c$	$P2_1/c$	*Pbca*	*Pbca*
a, Å	10.0550(7)	10.453(2)	6.9917(7)	11.3060(7)	11.5811(4)
b, Å	24.6237(17)	6.7887(14)	12.7918(13)	9.6081(6) A	9.9759(4)
c, Å	7.1837(5)	15.826(3)	14.4662(14)	18.9691(13)	18.7435(14)
α, deg	90	90	90	90	90
β, deg	90	95.947(5)	103.212(2)	90	90
γ, deg	90	90	90	90	90
V, Å^3	1778.6(2)	1117.0(4)	1259.6(2	2060.6(2)	2165.5(2)
Z	8	4	4	8	8
d_{calc}, g/cm^3	1.473	1.363	1.346	1.246	1.271
μ, mm^{-1}	0.108	0.084	0.083	0.078	0.079
Crystal size, mm	0.25×0.20×0.10	0.88×0.08×0.04	0.23×0.21×0.11	0.35×0.19×0.18	0.40×0.40×0.10
Measured reflections	14109	8347	10474	16492	42488
Independent reflections (R_{int})	1751 (0.0265)	1968 (0.0833)	2460 (0.0555)	2025 (0.0361)	3145 (0.0544)
T_{max}/T_{min}	0.9893/0.9736	0.9966/0.9294	0.9910/0.9813	0.9861/0.9732	0.9921/0.9691
R_1/wR_2 [$I > 2\sigma(I)$]	0.0364/0.0957	0.0869/0.1568	0.0719/0.1665	0.0726/0.1746	0.0408/0.1041
R (all data)	0.0440/0.1007	0.1312/0.1716	0.0914/0.1753	0.0948/0.1854	0.0549/0.1102
Residual electron density, e/Å^3	0.410/–0.169	0.558/–0.215	0.578/–0.208	0.426/–0.354	0.329/–0.185
GOF	1.047	1.141	1.104	1.077	1.043

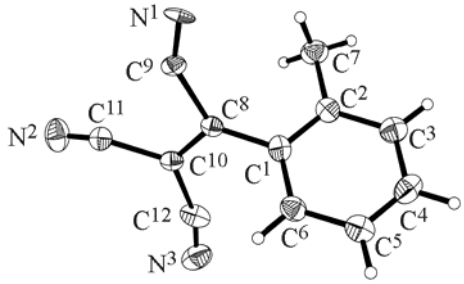
Complexes **2a–2g** were transformed into the metal-free bases **3a–3g** via treatment with trifluoroacetic acid. That stage was required in view of the unwanted influence of Yb^{3+} on the potential photodynamic properties of the porphyrazines. Indeed, the energy consumption of the excited triplet state of the macrocycle due to its transfer to the luminescent levels of ytterbium ion via the Förster dipole-dipole exchange can result in the undesired competition with the energy consumption on the bimolecular formation of active oxygen forms.

Similarly to the case of the metal complexes, electron absorption spectra of compounds **3a–3g** contained the Soret and *Q* bands typical of the porphyrazines (Table 3). In the low-viscosity organic media (THF, toluene, diethyl ether, ethyl and methyl alcohols, acetone, acetonitrile, DMSO, and DMF) the excitation of the studied porphyrazine dyes resulted in a very weak red fluorescence at 635–670 nm. It is interesting to note that the maximum of the *Q* band was shifted to longer wavelengths as compared to the corresponding metal complexes.

IR spectra of the free bases **3a–3g** contained no bands assignable to vibrations of the CN groups of the axial ligands; the absorption bands assigned to vibrations of NH groups were observed (Table 2).



3d



3g

Fig. 1. General view of molecules of aryltricyanoethylenes **3d** and **3g**.

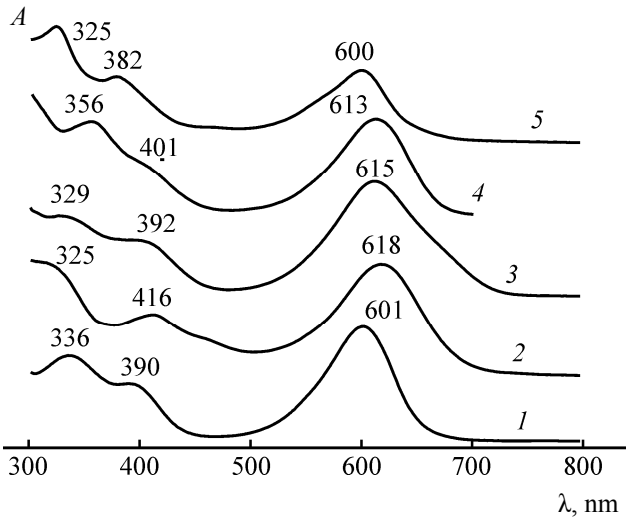


Fig. 2. (*1–5*) UV absorption spectra of complexes **2b–2g** in THF.

The special structural feature of the porphyrazine dyes prepared in this work was the alternation of electron-accepting (C≡N) and π-donating aromatic groups located at the macrocycle periphery and combined into a conjugate macrocyclic structure (π-spacer). The presence of donor and acceptor groups in the common π-conjugation system is a prerequisite for the intramolecular charge transfer from the donor to the acceptor at the light excitation of the dye molecule [7]. In turn, this may result in the intramolecular motion of the molecule fragments (rotation or twisting); therefore, such dyes are known as "molecular rotors." The light-induced intramolecular motion largely determines the photophysical properties of the molecular rotor, since it strongly affects the balance of populations of the radiative (fluorescent) and nonradiative (dark) states of the molecule: rotation or twisting of its fragments increases the population of the dark state. The possibility of the nonradiative consumption of energy of the excited molecule via the

Table 2. IR spectroscopy data for porphyrazine chromophores and aromatic derivatives of tricyanoethylene

Comp. no.	$\nu_{C\equiv N}$, cm^{-1}		Δν	ν_{NH} in porphyrazines **3**, cm^{-1}
	2	**1**		
a	2205, 2122	2234	29	3420
b	2202, 2129	2236	34	3450
c	2208, 2143	2238	30	3460
d	2199, 2110	2227	28	3443
e	2198, 2122	2237, 2225	39	3424
f	2201, 2136	2240	39	3424
g	2197, 2132	2237, 2222	40	3426

Table 3. Electron absorption and fluorescence spectral data for complexes **3a–3g**

Complex	λ, nm[a]		λ^{fl}, nm[b]
	Cope	Q	
3a	328, 398	610	635
3b	329, 399	610	640
3c	325, 413	632	670
3d	330, 409	621	660
3e	350, 410	615	650
3f	382, 416	604	635
3g	407, 458	590, 619	640

[a] Solution in THF. [b] λ_{ex} = 580 nm, $c = 5\times10^{-5}$ mol/L.

intramolecular motion is facilitated in the low-viscosity media. Hence, the fluorescent properties of the dye are deteriorated in the low-viscosity media. On the contrary, the intramolecular motion is hindered in the high-viscosity surrounding, thus sharply enhancing the fluorescence and changing its quantum yield and lifetime [7–10]. It should be noted that the dependence of the fluorescence parameters of molecular rotors on the medium viscosity can be expressed by the equations derived theoretically and verified experimentally [7, 8]. In particular, the Förster–Hoffmann equation (1) relates the fluorescence quantum yield Φ and the solvent viscosity η, z and α being constant parameters [8].

$$\Phi = z\eta^{\alpha}. \quad (1)$$

Similar equation (2) has been derived for another fluorescence parameter, lifetime τ [8] (k_r being the rate constant of the radiative transition).

$$\log \tau = \log (z/k_r) + \alpha \log \eta. \quad (2)$$

The availability of simple equations relating the dye fluorescence parameters with the medium viscosity opens the possibility of application of the fluorescent molecular rotors as sensors of the local viscosity. In particular, viscosity properties of microscopic elements of biological objects (cells and tissues) can be thus measured.

Our recent paper [9] presented a solid photophysical proof that the discussed tetrapyrrole dyes were in fact fluorescent molecular rotors that could be utilized to determine the local intracellular viscosity (even under conditions of its dynamic change, for example, under conditions of photodynamic therapy) using tetra(4-fluorophenyl)tetracyanoporphyrazine **3b** as an example.

Similarly, the estimations performed in this work revealed the strong dependence of the fluorescence quantum yield on the medium viscosity. The Förster–Hoffmann equation was valid for almost all of the considered tetraaryltetracyanoporphyrazines (Fig 3).

The slope of the corresponding linear curves can be used as a quantitative merit of the fluorescence parameters sensitivity to viscosity. For the molecular rotors this value ranges between 1/3 and 2/3 [10].

For the porphyrazine macrocycles studied in this work the slope ranged between 1/3 and 1/2; hence, they could be considered fluorescent molecular rotors.

It is important to note that the slope of the curve was lower (evidencing the weaker dependence of the quantum yield on the viscosity) in the cases of porphyrazines **3c** and **3f** containing *ortho*-substituted peripheral phenyl groups. It is known that *ortho*-substituents in the aromatic ring sterically hinder the intramolecular motion of the aryl group. This can be the reason of reduction of the sensitivity of the fluorescent properties of porphyrazines **3c** and **3f** to viscosity. A similar effect has been observed for 4,4'-difluoro-4-bora-3a,4a-diaza-*s*-indacene molecular rotor upon introduction of *ortho*-methyl groups in the phenyl fragment [10]. Hence, we suppose that the rotor properties of tetraaryltetracyanoporphyrazines **3a**–**3f** originated from the photoinduced rotation of the aryl groups (twisting about the C–C bond of the aromatic ring and the macrocycle) at the molecule excitation at the *Q* band wavelength. Interestingly, the porphyrazine **3g** containing two methyl groups in the *ortho*-positions of the benzene ring exhibited no noticeable influence of the medium viscosity on the fluorescence quantum yield.

Using porphyrazine **3b** as an example we calculated the fluorescence lifetime at different medium viscosities (Table 4). The results evidenced a sharp increase in the fluorescence lifetime with the increase in the medium viscosity. A special feature of the fluorescence of the studied porphyrazines was its biexponential decay, pointing at the presence of two radiative sites in the solution, differing in the fluorescence decay time (τ_1 and τ_2).

Interestingly, the contribution of the short-living radiative centers (α) to the observed fluorescence of porphyrazine **3b** was noticeably decreased with the increase in the solution viscosity. Fluorescent rotor dissolved in a homogeneous medium can be characterized by the average lifetime of fluorescence (τ_{av}) defined by equation (3).

$$\tau_{av} = \frac{\Sigma a_i^2 \tau_i^2}{\Sigma a_i \tau_i}. \quad (3)$$

We obtained the correlation curves relating the average fluorescence lifetime with the solution viscosity (Fig. 4) for the selected porphyrazine dyes (including the metal complex **2b**). The data shown in Fig. 4 followed the Förster–Hoffmann equation for the three studied dyes. In terms of the slope of the curves as a measure of the fluorescence sensitivity to viscosity, the considered complexes exhibited the viscosity sensitivity close to the highest known for molecular rotors so far (≈2/3) [10]. Note that the

presence of the central cation as well as the introduction of naphthyl peripheral substituents instead of *para*-fluorophenyl ones did not significantly alter the rotor properties of the porphyrazine macrocycle.

The viscosity of the dye solution can be estimated from the red fluorescence decay time using the obtained correlation curves. As far as possible biomedical applications are concerned, this approach can lead to a development of the methods for microviscometry measurements inside the living cells without knowledge of the local dye concentration in the cell elements, since the fluorescence lifetime is independent of the phosphor concentration.

We have earlier demonstrated the high photocytotoxicity of porphyrazine **3b** [9]. Using the cell cultures, we have shown the high efficiency of this compound as sensitizer of photodynamic therapy owing to the generation of singlet oxygen at photo-excitation. In this work we confirmed the photo-cytotoxicity of porphyrazine **3d** to cancer cells. This porphyrazine is of special interest in view of biomedical applications, since the maxima of its *Q* band and the emission band are shifted towards longer wavelengths, and the broad far-red absorption band strongly overlaps the so-called first optical window of the relative transparency of the biological tissue suitable for the in vivo imaging (650–950 nm) [11, 12]. It is this spectral range where most of the photosensitizers applicable in modern clinical diagnostics operate. This spectral feature of porphyrazine **3d** is especially characteristic of aqueous solutions, making this compound promising for biomedical studies. It should be noted that porphy-razine **3c** containing pentafluorophenyl substituents is interesting as well for the same reason. However, as follows from the data in Fig. 3, its fluorescence is weaker as compared to compound **3d**, viscosity being the same.

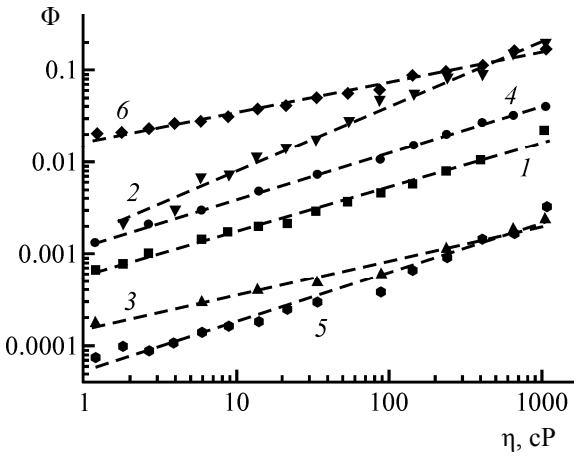


Fig. 3. Quantum yield of fluorescence (excitation at the *Q* band maximum) of porphyrazines **3a–3g** (*1–6*) as a function of the ethanol–glycerol mixture viscosity. The slopes (α_{rotor}): 0.3 (**3c**, **3f**), 0.4 (**3a**, **3d**, **3e**), 0.5 (**3b**).

The experiments with the T-24 cells culture (human urinary bladder carcinoma, ATCC HTB-4) revealed rapid, within minutes of incubation, delivery of porphyrazine **3d** into the cells and its accumulation in cytoplasm in the vicinity of the cell nucleus. The dye was most likely localized at the intracellular membranes, in particular, endoplasmic reticulum and nucleus shell. The latter fact is of special importance in view of the potential application of the discussed compounds as photosensitizers, since the cell nucleus is the most sensitive to photoinduced degradation.

The irradiation of the cell culture (wavelength 615–635 nm, dose 10 J/cm^2, light-emitting diode [13]) after 4 h of incubation with porphyrazine **3d** resulted in the photoinduced cells death. The strength of the photodynamic effect was a function of the dye concentration (Fig. 5). At the same time, the toxicity of the dye in the dark was not observed.

Table 4. Calculated lifetimes of porphyrazine **3b** fluorescence

Mixture composition		Viscosity, cP	τ_1, ns	α_1, %	τ_2, ns	α_2, %	τ_{av}, ns
MeOH	glycerol						
0	100	960	0.49	18.01	1.62	81.99	1.55
10	90	346	0.31	25.18	0.99	74.82	0.93
20	80	140	0.17	31.34	0.55	68.66	0.50
30	70	54	0.07	37.81	0.27	62.19	0.24
40	60	24	0.03	59.98	0.15	40.02	0.12

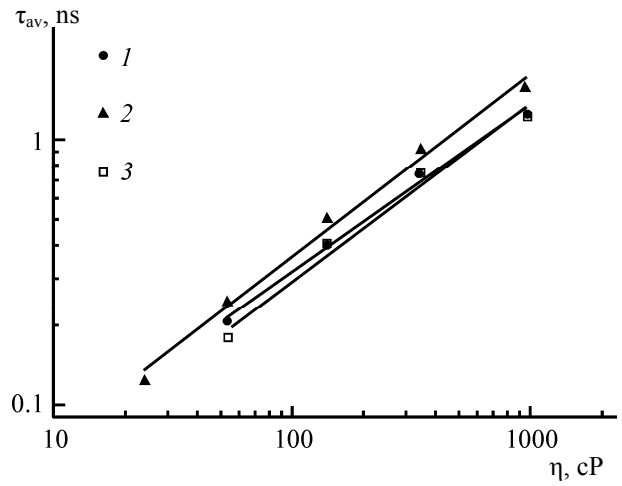


Fig. 4. Correlation curves of the fluorescence lifetime dependence on the solution viscosity. The slopes: 0.63±0.03 (**2b**, ●), 0.69±0.04 (**3b**, ▲), 0.67±0.04 (**3d**, □).

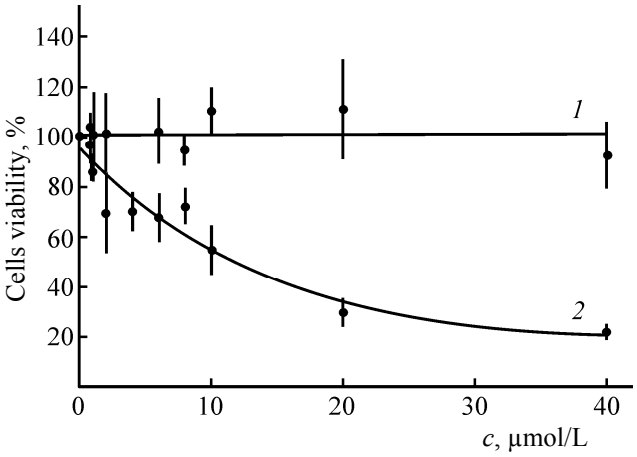


Fig. 5. Viability of T-24 cells incubated during 4 h with porphyrazine **3d** at different concentrations (*1*) in the dark and (*2*) at illumination (10 J/cm^2, 615–635 nm).

To conclude, the template assembly has afforded a series of new porphyrazine macrocycles in the form of free bases. Using different aryltricyanoethylenes as building blocks has allowed a variation of the peripheral structure of the macrocycles and a fine tuning the photophysical properties of the prepared products. Quantum yield and lifetime of fluorescence of the obtained porphyrazines are highly sensitive to the medium viscosity (including biological systems). The prepared porphyrazines are promising sensitizers for photodynamic therapy.

EXPERIMENTAL

IR spectra of the compounds in the form of mineral oil suspensions were recorded using an FSM 1201 spectrometer. UV-vis electron absorption spectra were recorded using a Perkin Elmer Lambda 25 spectrometer. ^{1}H NMR spectra were recorded using a Bruker Avance DPX-200 instrument (200 MHz) at 25°C. Fluorescence was studied in a stationary mode using a Perkin Elmer LS 55 spectrometer at 300–800 nm. Mass spectra (MALDI TOF) were recorded using a Bruker Microflex LT spectrometer.

Dynamic viscosity of the binary ethanol(methanol)–glycerol mixtures was measured using an SVM 3000 Stabinger viscometer (Anton Paar) with accuracy of ±0.35%. The porphyrazines solutions were prepared via mechanical mixing with ultrasonication during at least 15 min.

Fluorescence decay curves of the solutions were recorded in 10 mm quartz cells using time-correlated single photon counting (TCSPC) method with a DeltaFlex TCSPC Horiba system. The specimens were excited at 635 nm using a NanoLED impulse laser (200 ps pulses). The decay curves were recorded at the peak value of the counted photons equal to 1000. Temperature of the solutions was precisely set using a RE104 thermostat (Lauda Technology Ltd).

X-ray diffraction analysis was performed using Bruker AXS SMART APEX (**1b**, **1d**, **1e**, and **1f**) and Oxford Xcalibur Eos (**1g**) automated diffractometers (graphite monochromator, MoK_α radiation, ω-scanning, λ 0.71073 Å). The structures were solved via the direct method using SHELXTL software package and refined via the full-matrix least-squares method over F^2_{hkl} under anisotropic approximation for the non-hydrogen atoms. The extinction was accounted for using SADABS (**1b**, **1d**, **1e**, and **1f**) and SCALE3 ABSPACK (**1g**) software. The single crystals were obtained via recrystallization from toluene. Basic crystallographic data and parameters of the structure refinement are listed in Table 1.

Intracellular distribution and photocytotoxicity of porphyrazine **3d** were studied using T-24 cell culture (human urinary bladder carcinoma, reference number ATCC® HTB-4™) from the collection of Scientific Research Institute of Virology, Russian Academy of Medical Sciences. The cells were cultured in an Igla MEM (PanEko, Russia) medium containing 10% of embryonic calf serum (HyClone, USA) and 2 mM of L-glutamine (PanEko, Russia). The culturing was performed in a CO_2 incubator at 37°C under atmo-

sphere of 5% CO_2, each passaging was accompanied by treatment with 0.25% solution of trypsin–EDTA (PanEko, Russia).

Viability of the cells culture was estimated using MTT test [14]. The cells were seeded into the wells of a 96-well microplate (3000 cells per a well) and incubated overnight. The medium in the wells was then changed for 200 μL of the growth medium containing different concentrations of porphyrazine **3d**, and the cells were incubated during 4 h; the medium was then again changed for the fresh growth medium.

The cells in the 96-well microplate were illuminated during 24 h using a radiation element with an exchangeable light diode matrix providing for a uniform illumination [13]. The radiation dose was 10 J/cm^2 (615–635 nm), the power density being 20 mW/cm^2. After the illumination, 3(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2*H*-tetrazolium bromide (MTT reagent, Alfa Aesar, Great Britain) was introduced to the medium to the final concentration of 0.5 mg/mL, and the cells were incubated during 4 h. The medium was then removed, and the crystals of colored MTT formazan were dissolved in 200 μL of dimethylsulfoxide. The absorbance of the solutions in the wells was measured using a Synergy MX microplate reader (BioTek, USA) at 570 nm. Viability of the cells was estimated from the absorbance of the solutions in the wells relative to that in the reference well (not illuminated). The illumination stage was omitted for determination of the dark cytotoxicity.

Synthesis of the compounds and their analysis were carried out using anhydrous solvents. *N*-Chlorosuccinimide, *p*-fluorobenzaldehyde, pentafluorobenzaldehyde, β-naphthalene carboxaldehyde, 4-biphenyl car-boxaldehyde, *o*-methylbenzaldehyde, and 2,6-xylene carboxaldehyde were commercial substances (Acros organics and P&M-Invest). Bisindenylytterbium was prepared as described elsewhere [15].

Aryltricyanoethylenes **1a**–**1g** were prepared as described in [5]. Spectral and elemental analysis data for 2-phenyl-1,1,2-tricyanoethylene (**1a**), 2-(4-fluorophenyl)-1,1,2-tricyanoethylene (**1b**), 2-(pentafluorophenyl)-1,1,2-tricyanoethylene (**1c**), and 2-(2-methylphenyl)-1,1,2-tricyanoethylene (**1f**) have been given in [4], [16], [5], and [9], respectively.

2-(2-Naphthyl)-1,1,2-tricyanoethylene (1d). IR spectrum, ν, cm^{-1}: 2227 (C≡N). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 8.65 s (1H), 8.21 m (2H), 8.09 m (2H), 7.77 m (2H). Found, %: C 79.69; H 3.11; N 18.20. $C_{15}H_7N_3$. Calculated, %: C 78.59; H 3.08; N 18.33.

2-(4-Biphenyl)-1,1,2-tricyanoethylene (1e). IR spectrum, ν, cm^{-1}: 2237, 2225 (C≡N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.14 d (2H, *J* 8.5 Hz), 7.85 d (2H, *J* 8.4 Hz), 7.64 m (2H), 7.51 m (3H). Found, %: C 80.31; H 3.47; N 16.22. $C_{17}H_9N_3$. Calculated, %: C 79.99; H 3.55; N 16.46.

2-(2,6-Dimethylphenyl)-1,1,2-tricyanoethylene (1e). IR spectrum, ν, cm^{-1}: 2237, 2222 (C≡N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.25 m (3H), 2.36 s (6H). Found, %: C 75.49; H 4.45; N 20.06. $C_{13}H_9N_3$. Calculated, %: C 75.35; H 4.37; N 20.28.

Tetraphenyltetracyanoporphyrazine (**3a**), tetra-(*p*-fluorophenyl)tetracyanoporphyrazine (**3b**), tetra(*o*-methylphenyl)tetracyanoporphyrazine (**3f**), and their complexes with ytterbium have been obtained earlier [4, 9, 16].

Ytterbium tetra(2-naphthyl)tetracyanoporphyrazinate (2d). A solution of 1.15 g (4.50 mmol) of 2-(2-naphthyl)-1,1,2-tricyanoethylene **1d** in 7 mL THF degassed in a vacuum was added in small portions to a solution of 0.52 g (0.90 mol) of bisindenyl ytterbium(II) π-complex in 3 mL THF; black precipitate was formed. The mixture was left standing for 1 day and then filtered in a vacuum. The unreacted compound **1d** and its com-plex were removed via washing with degassed toluene till discoloration. The isolated product was refluxed in toluene in air during 24 h. The non-dissolved pre-cipitate was separated and dried at a reduced pressure. Yield 47%. IR spectrum, ν, cm^{-1}: 2199 (C≡N); 1621, 1595, 1571, 1509, 1494 (C=N, C=C), 903, 862, 840, 814, 766, 750, 730, 710, 695, 630, 618 (C–H_{Ar}). Found, %: C 62.44; H 2.99; N 14.86; Yb 14.98. $C_{60}H_{33}N_{12}O_3Yb$. Calculated, %: C 63.05; H 2.91; N 14.70; Yb 15.14.

Ytterbium tetra(pentafluorophenyl)tetracyanoporphyrazinate (2c) was prepared similarly. Yield 85%. IR spectrum, ν, cm^{-1}: 2208 (C≡N), 1650, 1521, 1500, 1416 (C=N, C=C), 1218, 1185, 1128, 1112 (C–F). Mass spectrum, *m*/*z*: 1285 [*M*]$^-$. Found, %: C 40.75; F 29.05; N 13.08; Yb 13.24. $C_{44}H_5F_{20}N_{12}O_3Yb$. Calculated, %: C 40.57; F 29.17; N 12.90; Yb 13.28.

Ytterbium tetra(4-biphenyl)tetracyanoporphyrazinate (2e) was prepared similarly. Yield 42%. IR spectrum, ν, cm^{-1}: 2198 (C≡N), 1656, 1598, 1574, 1502 (C=N, C=C), 907, 820, 798, 764, 752, 733, 697 (C–H_{Ar}). Found, %: C 64.95; H 3.40; N 13.45; Yb 14.20. $C_{68}H_{41}N_{12}O_3Yb$. Calculated, %: C 65.49; H 3.31; N 13.48; Yb 13.88.

Ytterbium tetra(2,6-dimethylphenyl)tetracyanoporphyrazinate (2g) was prepared similarly. Yield 42%. IR spectrum, ν, cm^{-1}: 2197 (C≡N), 1652, 15602, 1569, 1495 (C=N, C=C), 905, 817, 771, 747, 705 (C–H_{Ar}). Found, %: C 57.55; H 3.43; N 16.51; Yb 17.60. $C_{48}H_{33}N_{12}O_3Yb$. Calculated, %: C 57.71; H 3.33; N 16.83; Yb 17.32.

Tetra(2-naphthyl)tetracyanoporphyrazine (3d). Ytterbium tetra(2-napthyl)tetracyanoporphyrazinate **2d** (0.2 g, 0.22 mmol) was dissolved in 2 mL of trifluoroacetic acid and stirred during 30 min at room temperature. About 30 mL of water was then added; the precipitate was centrifuged off and washed with water till neutral reaction. The product was purified by column chromatography (silica gel 60, 40–60 μm, THF as eluent). Yield 38%. IR spectrum, ν, cm^{-1}: 3443 (N–H), 2200 (C≡N), 1595, 1508, 1496, 1469, 1451, 1435 (C=C, C=N), 902, 864, 839, 814, 749, 617 (C–H_{Ar}). Mass spectrum, *m*/*z* 918 $[M]^+$. Found, %: C 78.78; H 3.19; N 18.03. $C_{60}H_{30}N_{12}$. Calculated, %: C 78.42; H 3.29; N 18.29.

Tetra(pentafluorophenyl)tetracyanoporphyrazine (3c) was prepared similarly. Yield 33%. IR spectrum, ν, cm^{-1}: 3460 (N–H), 2207 (C≡N), 1650, 1523, 1501, 1468, 1414 (C=C, C=N). Mass spectrum, *m*/*z*: 1078 $[M]^+$. Found, %: C 49.55; H 0.21; F 34.78; N 15.46. $C_{44}H_2F_{20}N_{12}$. Calculated, %: C 49.00; H 0.19; F 35.23; N 15.58.

Tetra(4-biphenyl)tetracyanoporphyrazine (3e) was prepared similarly. Yield 35 %. IR spectrum, ν, cm^{-1}: 3422 (N–H), 2201 (C≡N), 1603, 1558, 1499 (C=C, C=N), 906, 855, 823, 765, 750, 738, 698 (C–H_{Ar}). Mass spectrum, *m*/*z*: 1022 $[M]^+$. Found, %: C 79.42; H 3.84; N 16.74. $C_{68}H_{38}N_{12}$. Calculated, %: C 79.83; H 3.74; N 16.43.

Tetra(2,6-dimethylphenyl)tetracyanoporphyrazine (3g) was prepared similarly. Yield 30%. IR spectrum, ν, cm^{-1}: 3426 (N–H), 2193, 2227 (C≡N), 1613, 1567, 1555, 1505 (C=C, C=N), 906, 796, 777, 753, 688, 675 (C–H_{Ar}). Mass spectrum, *m*/*z*: 830 $[M]^+$. Found, %: C 75.55; H 4.70; N 19.75. $C_{52}H_{38}N_{12}$. Calculated, %: C 75.16; H 4.61; N 20.23.

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