Pyrazinoporphyrazines with Externally Appended Pyridine Rings. 13. Structure, UV-visible Spectral Features and Noncovalent Interaction with DNA of a Positively Charged Binuclear (Zn^{II}/Pt^{II}) Macrocycle with Multimodal Anticancer Potentialities

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Supporting Information

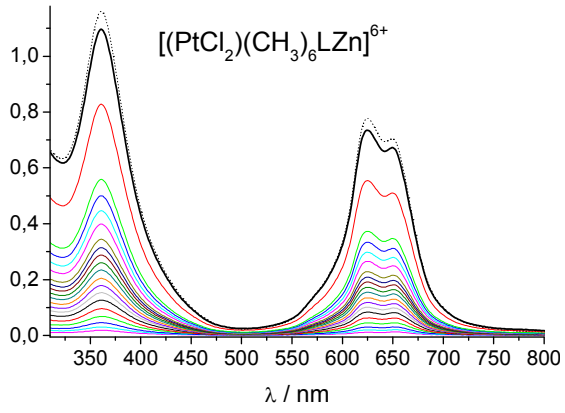
S1) Aggregation of $[(PtCl_2)(CH_3)_6LZn]^{6+}$ and $[(CH_3)_8LZn]^{8+}$ in pure water.

S2) Global analysis of equilibrium multiwavelength spectroscopic data with Singular Value Decomposition (SVD) and non linear regression modelling.

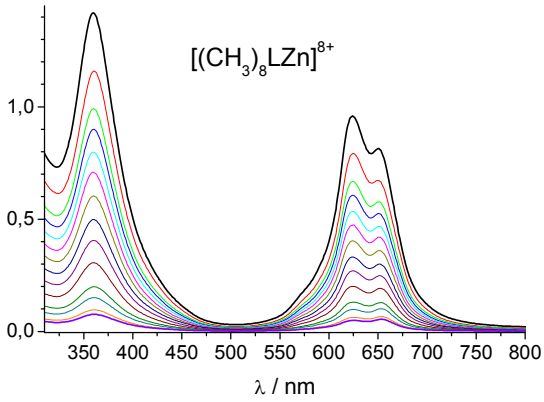
S3) Cartesian coordinates for the optimized structures of $[(PtCl_2)(CH_3)_6LZn]^{6+}$.

S1) Aggregation of $[(PtCl_2)(CH_3)_6LZn]^{6+}$ and $[(CH_3)_8LZn]^{8+}$ in pure water

In order to determine the dimerization constant of the (Zn^{II}/Pt^{II}) porphyrazine hexacation $[(PtCl_2)(CH_3)_6LZn]^{6+}$ and its octacationic analogue $[(CH_3)_8LZn]^{8+}$ in water, we performed dilution experiments monitored spectrophotometrically. See Figure S1 for the results. Successful application of a global analysis method (SPECFIT/32 program, see section S3) required the spectrum of the monomer was fixed in the calculation. This spectrum was determined, as mentioned in the main text, by registering the corrected excitation spectrum (up to 680 nm) for the emission wavelength λ_{em} = 690 nm in pure water. We then assigned to the absorption spectrum of the monomer, the only emitting species in the system, the profile of the excitation spectrum. At the maximum wavelength of 656 nm we attributed the ε_{max} experimentally obtained in the presence of SDS, suitably corrected to take into account that the FWHM of the Q-band of the ligand in water is slightly larger than that in the presence of SDS. To this purpose gaussian profiles and normalized integrals for the Q-band in absence and presence of SDS were assumed. In this way the epsilon values of the monomer in water at all the wavelengths were retrieved. The absorption spectrum, so obtained, was fixed in the global analysis of the UV-vis spectral data sets relevant to monomer-dimer equilibrium in Figure S1a and b. We thus determined the dimerization constants, pK_d, 6.99 and 7.12 for the hexacation and octacation, respectively, and the associated spectra of the respective dimers (Figure S1c and d).



a



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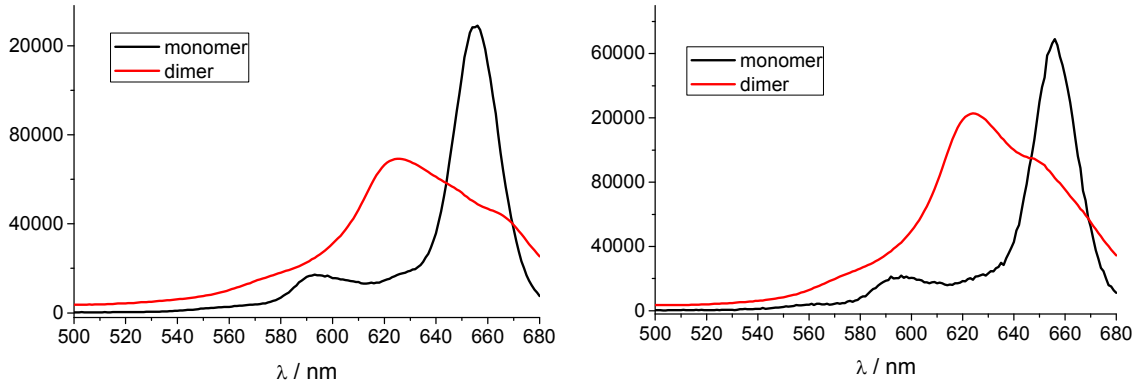

c d

Figure S1. Absorption spectra of water solutions of (a) $[(PtCl_2)(CH_3)_6LZn]^{6+}$ at concentrations from 2×10^{-5} M to 3×10^{-7} M and (b) $[(CH_3)_8LZn]^{8+}$ at concentrations from 1.6×10^{-5} M to 0.9×10^{-6} M; T=295 K, cell pathlength 1 cm. Absolute spectra of monomer (fixed) and dimer (optimized) in the global analysis of dilution data corresponding to (c) $\log (K_d/M^{-1}) = 6.99$ for $[(PtCl_2)(CH_3)_6LZn]^{6+}$ and (d) $\log (K_d/M^{-1}) = 7.12$ for $[(CH_3)_8LZn]^{8+}$.

The dimerization constants for the two compounds are somewhat higher than those reported previously.[1] We believe the present values are more reliable.

S2) Global analysis of equilibrium multiwavelength spectroscopic data with Singular Value Decomposition (SVD) and non linear regression modelling

This application was performed using the commercial SPECFIT/32^{TM} program, based on the publications of A. Zuberbühler.[2] Multiwavelength spectroscopic equilibrium data sets are arranged in matrix form **Y**, where a number Nw of wavelengths and a number Nm of corresponding measured spectroscopic signals are ordered in columns, whereas ligand and receptor concentrations are inserted in rows. Thus each element of the data matrix Y_{ij} corresponds to a wavelength j and an experimental quantity (absorbance, circular dichroism, fluorescence intensity) for a given couple of concentrations i of ligand and receptor (typically in our experiments one of them is kept constant). A least square best estimator **Y'** of the original data **Y** is reconstructed as the eigenvector representation **Y'** = **U×S×V**, where **S** is a vector that contains the relative weights of the significant eigenvectors (Ne, number of significant eigenvectors), **U** is a matrix (Nm×Ne) of concentration eigenvectors ($U^T\times U=1$, orthonormal) and **V** (Ne×Nw) is a matrix of spectroscopic eigenvectors ($V\times V^T$, orthonormal). This **Y'** matrix contains less noise than **Y** because the SVD procedure can factor random noise from the principal components. This reconstructed data matrix **Y'** is utilized in

the global fitting instead of the original data matrix **Y**. Complexation equilibria are solved assuming a complexation model (i.e. contemporary presence of a number of complexes of given stoichiometries in equilibrium with free species in solution) and optimizing the numeric combination of all the spectroscopic contributions to best reproduce the **Y'** signals. The analysis relies mainly on absorption data but also fluorescence data may be analysed, provided they are relevant to optically thin samples (linear dependence of fluorescence on concentration for all the species involved). Given the direct linearity between absorbance and concentration and the relation that must exist between the concentrations of the various species in the postulated simultaneous equilibria, the program calculates the conditional association constants and the spectra of the complexes based on a non-linear least square fit, using the Levenberg-Marquardt algorithm to best reproduce the experimental data for all the explored wavelengths and ligand-receptor concentration couples. The fits were evaluated on the basis of their Durbin-Watson (DW) factors and the relative error of fit. The DW test is very useful to check for the presence of auto-correlation in the residuals. This method is recommended for systematic misfit errors that can arise in titration experiments. It examines the tendency of successive residual errors to be correlated. The Durbin-Watson statistics ranges from 0.0 to 4.0, with an optimal mid-point value of 2.0 for uncorrelated residuals (i.e., no systematic misfit). In contrast to the χ^2 (Chi-squared) statistics, which requires the noise in the experimental data is random and normally distributed, the DW factor is meaningful even when the noise level in the data set is low. Since the factorized data usually have a significantly lower noise level than the original data, DW test is ideal for the present type of data.

We applied this method to analyze the concentration dependent absorption spectra for the dimerization equilibrium of $[PtCl_2)(CH_3)_6LZn]^{6+}$ and $[(CH_3)_8LZn]^{8+}$ and for titration of $[PtCl_2)(CH_3)_6LZn]^{6+}$ and $[(CH_3)_8LZn]^{8+}$ with duplex DNA. In the latter cases several binding models were tested, all including the dimerization equilibrium of the porphyrazines. From analysis of the titration data of Figure 5a and 5b in the main text the best complexation model on the basis of the DW factors resulted to be that with 1:1, 2:1 and 4:1 ligand:duplex complexes. The dimerization

constant and the spectra of both monomer and dimer were fixed in the calculation. The spectrum of the 1:1 complex was also fixed (see main text for its calculation). The experimental data for $[PtCl_2)(CH_3)_6LZn]^{6+}$ were best reproduced with the binding constants $\log(K_{11}/M^{-1}) = 5.85 \pm 0.03$, $\log(K_{21}/M^{-2}) = 13.96 \pm 0.05$ and $\log(K_{41}/M^{-4}) = 27.53 \pm 0.15$. For $[(CH_3)_8LZn]^{8+}$ the data were best reproduced with binding constants $\log(K_{11}/M^{-1}) = 5.84 \pm 0.08$, $\log(K_{21}/M^{-2}) = 14.30 \pm 0.14$ and $\log(K_{41}/M^{-4}) = 28.18 \pm 0.35$. In Figure 5 of the main text the pure spectra (c,d) and the evolution of the concentrations (e,f) of all the species in solution are reported. The quality of the agreement between the experimental data and the best fits is shown in Figure S2.

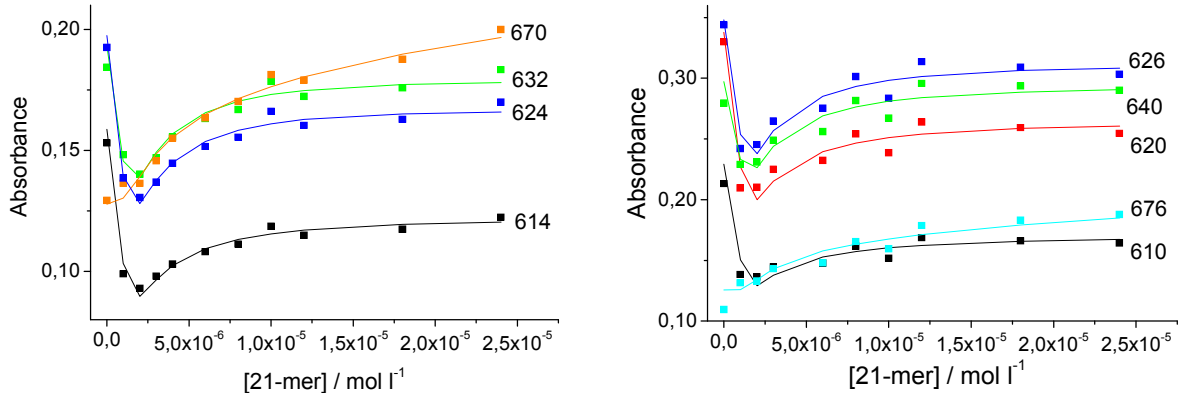

Figure S2. Absorbance at key wavelengths of a 6×10^{-6} M solution of (a) $[(PtCl_2)(CH_3)_6LZn]^{6+}$ and (b) $[(CH_3)_8LZn]^{8+}$, in presence of increasing DNA concentration $(0.1\text{-}2.4)\times10^{-5}$ M in TRIS/KCl buffer of pH 7.4 at 295 K, d = 1 cm; Symbols are experimental values; lines represent best fit values corresponding to $\log(K_{11}/M^{-1}) = 5.85$, $\log(K_{21}/M^{-1}) = 13.96$, $\log(K_{41}/M^{-2}) = 27.53$ for $[(PtCl_2)(CH_3)_6LZn]^{6+}$ and $\log(K_{11}/M^{-1}) = 5.84$, $\log(K_{21}/M^{-2}) = 14.30$ and $\log(K_{41}/M^{-4}) = 28.18$ for $[(CH_3)_8LZn]^{8+}$.

Bibliography

1. I. Manet, F. Manoli, M. P. Donzello, E. Viola, G. Andreano, A. Masi, L. Cellai and S. Monti, *Org. Biomol. Chem.*, 2011, **9**, 684-688; I. Manet, F. Manoli, M. P. Donzello, C. Ercolani, D. Vittori, L. Cellai, A. Masi and S. Monti, *Inorg. Chem.*, 2011, **50**, 7403-7411.
2. H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbuhler, *Talanta*, 1985, **32**, 257-264; H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbuhler, *Talanta*, 1985, **32**, 95-101.

S3) Cartesian coordinates for the optimized structures of $[(PtCl_2)(CH_3)_6LZn]^{6+}$.

Note: *u* = up; *d* = down

Structure 1 (uu orientation of the methyl groups)

ATOMS

Zn	0.00000	0.00000	0.00000
C	4.19518	0.70528	-0.02977
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C	0.70987	-4.18839	0.24815
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C	4.19802	-0.69788	0.02977
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Structure 2 (dd orientation of the methyl groups)

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C	0.70846	-4.19435	0.02172
C	-4.19679	0.70526	-0.03297
C	-0.70486	-4.19839	0.02166
C	4.19434	-0.69827	0.12748
C	0.70771	4.18792	-0.23040
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N	-1.42174	5.30889	-0.32703
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H	-3.77256	-10.84736	-0.19851
H	-10.76076	-3.78085	0.92634
H	3.83090	-10.79795	0.28831
H	10.83595	3.76189	0.25503
H	-3.74969	10.84600	-0.21634
H	9.20672	-4.12959	-1.25072
H	2.54711	10.04090	-2.53285
H	-10.32737	2.27533	-1.87026
H	-2.36621	-10.17783	-2.15588
H	-9.17136	-4.21984	-0.95096
H	4.16759	-9.06828	-1.48343
H	9.22031	3.95110	-1.67616
H	-4.05849	9.08958	-1.96648
H	7.16514	-2.67573	-1.39838
C	0.99977	8.02855	-2.80396
C	-8.32807	0.74018	-2.23952
C	-0.82893	-8.16701	-2.44185
C	-7.08707	-2.95850	-1.65940
C	2.87314	-6.93979	-1.95953
H	7.16876	2.50418	-1.66342
C	-2.78775	6.92732	-2.35626
Pt	8.23887	0.13345	2.72591
Cl	7.88693	-1.44834	4.41311
Cl	7.90883	1.89082	4.23316
H	0.48543	-8.47187	1.71454
H	-8.33700	-0.36876	1.98342
H	-0.50095	8.48538	1.36842
H	3.44045	-7.47744	-2.72181
H	1.94221	-6.56235	-2.38841
H	3.46003	-6.10993	-1.55557
H	-7.67504	-3.57906	-2.33834
H	-6.75861	-2.05360	-2.17609
H	-6.21799	-3.50871	-1.28807
H	-3.32971	7.45485	-3.14365
H	-1.84969	6.53223	-2.75286
H	-3.39307	6.11105	-1.95184
H	-2.29952	-7.34047	1.86185
H	-1.34138	-8.61819	-3.29379
H	-0.79435	-7.08305	-2.57117
H	0.17875	-8.58908	-2.36743
H	-7.20050	2.39574	1.92570
H	-8.84508	1.21404	-3.07643
H	-7.25598	0.70848	-2.44596
H	-8.73397	-0.26642	-2.09400
H	2.19508	7.42365	1.61755
H	1.50999	8.50692	-3.64211
H	1.04080	6.94305	-2.92153
H	-0.03588	8.38256	-2.77076

END

Structure 3 (ud orientation of the methyl groups)

ATOMS

Zn	0.00000	0.00000	0.00000
C	4.19609	0.67564	-0.19255
C	-0.70857	4.01263	-1.23739
C	-4.19786	-0.67164	0.22233
C	0.70629	-4.01097	1.23156
C	-4.19813	0.68363	-0.18450
C	-0.70824	-4.00692	1.25330
C	4.19615	-0.66511	0.22627
C	0.70610	4.01475	-1.21868
N	5.31515	1.36933	-0.40992
N	-1.42799	5.08224	-1.56263
N	-5.31398	-1.36519	0.42515
N	1.43075	-5.08035	1.54488
N	-5.31448	1.37258	-0.40122
N	-1.42802	-5.07717	1.57517
N	5.31483	-1.35706	0.45045
N	1.43131	5.08586	-1.52467
C	6.45451	0.70686	-0.14047
C	-0.70824	6.17672	-1.87527
C	-6.45370	-0.68107	0.21211
C	0.71724	-6.17194	1.88064
C	-6.45407	0.68288	-0.20506
C	-0.70922	-6.17256	1.88578
C	6.45419	-0.65927	0.29469
C	0.71788	6.17751	-1.85966
C	-2.79491	1.08867	-0.31369
C	-1.13517	-2.66327	0.84856
C	2.79120	-1.07722	0.33829
C	1.12897	2.66815	-0.81889
C	2.79115	1.07958	-0.33089
C	-1.13576	2.66955	-0.83022
C	-2.79468	-1.07514	0.35565
C	1.12950	-2.66617	0.82573
N	-2.40454	-2.28891	0.73429
N	2.40120	-2.29256	0.70925
N	2.40078	2.29503	-0.70116
N	-2.40503	2.29933	-0.70244
N	-0.00268	-1.91953	0.61323
N	2.00593	0.00000	0.00000
N	-0.00341	1.92218	-0.60570
N	-2.01575	0.00768	0.02364
C	7.69436	1.48264	-0.43592
C	-1.49873	7.41148	-2.14679
C	-7.71279	-1.41626	0.52655
C	1.51356	-7.34676	2.33687
C	-7.71098	1.40834	-0.54742
C	-1.50359	-7.40960	2.13531
C	7.69368	-1.45973	0.51406
C	1.51789	7.35703	-2.29936
N	8.61222	-1.01650	1.41343
N	2.44218	7.90312	-1.44712
N	-8.00118	2.59435	0.07512
N	-2.45546	-7.41718	3.12134
C	-8.58098	-0.96130	1.51399
C	1.33928	-7.87573	3.61241
N	8.61208	1.65465	0.55224
C	-1.33871	8.54979	-1.36254
C	9.71173	-1.76581	1.66769
C	3.23217	8.92925	-1.85139
C	-9.09871	3.30902	-0.27846
C	-3.24537	-8.50373	3.30979
C	-9.71709	-1.69741	1.85185
C	2.14350	-8.92284	4.06238
C	9.71014	2.41263	0.31825
C	-2.13411	9.67580	-1.57558
C	9.94049	-2.97473	1.02052
C	3.13297	9.45783	-3.12823
C	-9.95988	2.86842	-1.27022
C	-3.11744	-9.63574	2.52130
C	-9.96941	-2.89411	1.18543
C	3.12537	-9.43133	3.21553
C	9.93808	3.01010	-0.91613
C	-3.09151	9.64374	-2.58657
C	9.00727	-3.43724	0.09309
C	2.19793	8.92435	-4.01197
C	-9.69233	1.66220	-1.91310
C	-2.15228	-9.65686	1.51735
C	-9.08868	-3.31740	0.20315
C	3.27025	-8.88789	1.94958
C	9.00669	2.83501	-1.93935
C	-3.22325	8.49763	-3.35365
C	7.86739	-2.67404	-0.15304
C	1.38998	7.86947	-3.58652
C	-8.56023	0.93582	-1.54328
C	-1.34563	-8.53400	1.33098
N	-7.98702	-2.59418	-0.11860
N	2.48153	-7.87104	1.51998
C	7.86817	2.07063	-1.69027
N	-2.44451	7.40788	-3.13893
H	10.40184	-1.36833	2.40844
H	3.93399	9.30700	-1.11159
H	-9.25694	4.23550	0.26830
H	-3.97022	-8.42830	4.11684
H	-10.38858	-1.33895	2.63117
H	2.00566	-9.32584	5.06505
H	10.39899	2.52897	1.15185
H	-2.00789	10.56028	-0.95217
H	10.84361	-3.53730	1.25281
H	3.78811	10.27993	-3.40998
H	-10.82825	3.47453	-1.52103

H	-3.77366	-10.48387	2.70710
H	-10.84048	-3.50647	1.41071
H	3.78079	-10.24611	3.51718
H	10.83893	3.60532	-1.05828
H	-3.73821	10.49389	-2.79485
H	9.16070	-4.38091	-0.43016
H	2.09851	9.31497	-5.02410
H	-10.34821	1.28964	-2.69913
H	-2.02806	-10.53080	0.87890
H	-9.23422	-4.23552	-0.36109
H	4.00885	-9.24699	1.23709
H	9.16019	3.29009	-2.91773
H	-3.94333	8.41231	-4.16371
H	7.10798	-3.00122	-0.86106
H	0.67374	7.41329	-4.26722
H	-8.30941	0.00817	-2.05421
H	-0.60685	-8.51229	0.53195
C	-7.09922	-3.11368	-1.19117
C	2.70010	-7.35895	0.14172
H	7.10992	1.91664	-2.45610
C	-2.64685	6.22509	-4.01587
Pt	8.33508	0.76338	2.35947
Cl	8.05030	-0.33435	4.40551
Cl	8.05149	2.84915	3.37941
H	0.59007	-7.43686	4.26843
H	-8.34383	-0.03929	2.04140
H	-0.60682	8.53664	-0.55732
H	3.24906	-8.12238	-0.41302
H	1.73431	-7.17538	-0.33636
H	3.27628	-6.43034	0.19095
H	-7.65538	-3.87085	-1.74681
H	-6.81833	-2.29481	-1.85947
H	-6.20416	-3.54895	-0.73719
H	-3.19795	6.55568	-4.89841
H	-1.67503	5.82232	-4.31424
H	-3.21437	5.46619	-3.46944
C	2.60809	7.39986	-0.05854
H	3.14798	8.15983	0.50929
H	1.62430	7.23235	0.38871
H	3.17306	6.46337	-0.08107
C	-7.13756	3.13450	1.15730
H	-7.71675	3.88092	1.70407
H	-6.84718	2.32342	1.83064
H	-6.24695	3.58830	0.71274
C	-2.65150	-6.24872	4.01832
H	-3.21528	-6.58825	4.88914
H	-1.67750	-5.86421	4.33359
H	-3.20361	-5.47237	3.48069

END

THE LOWEST THREE FREQUENCIES (CM^{-1}) ARE:

7.0; 13.0; 14.1.