ACTA CHEMICA IASI, **34_2**, 277-294 (2026)
DOI: 10.47743/achi-2026-2-0012

Article

CYCLODEXTRIN-ASSISTED PARTIAL DISAGGREGATION OF ZIRCONIUM PHTHALOCYANINES IN AQUEOUS MEDIA: SYNTHESIS AND PHOTOPHYSICAL CHARACTERIZATION

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Abstract: We report axially ligated zirconium phthalocyanines, $PcZr(L)_2$, bearing carboxylated chalcone ligands (L1–L3) and evaluate their photophysics across organic and aqueous media. The chalcones display solvent-governed absorption with large Stokes-shifted emission in DMSO but weak fluorescence in water. $PcZr(L)_2$ exhibits monomeric Soret/Q features in DMSO, whereas in aqueous/alkaline solutions it undergoes H-type aggregation, evidenced by Q-band hypsochromy, intensity loss, and growth of an ~640–644 nm band with quenched emission. Beer–Lambert linearity over the studied concentration ranges indicates that aggregation is predominantly solvent-induced rather than concentration-driven. Addition of cyclodextrins, particularly β-cyclodextrin and 2-hydroxypropyl-β-cyclodextrin, partially restores monomer-like spectral features in

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water, as indicated by increased Q-band intensity and enhanced fluorescence. These results suggest that cyclodextrin-based formulation is a simple non-covalent approach for improving the aqueous photophysical response of $PcZr(L)_2$ complexes without further modification of the phthalocyanine macrocycle.

***Keywords*:** Chalcones; Phthalocyanine complexes; Aggregation; Cyclodextrins; Fluorescence

Introduction

Phthalocyanines (Pc) and their metal complexes (PcM) are robust, π-conjugated macrocycles whose red–near-IR absorption, photostability, and modular chemistry underpin applications ranging from dyes and pigments to optoelectronics, photocatalysis, and photodynamic therapy (PDT). Tuning is possible at three levels: peripheral substituents on the macrocycle, the central metal (spin state, redox profile, coordination number), and, when the metal supports high coordination, axial/out-of-plane ligands that modulate solubility, aggregation, and intersystem crossing.[1]

Despite their utility, many PcM are poorly soluble in water and aggregate even when rendered water-dispersible. Aggregation alters the electronic structure and typically suppresses fluorescence and singlet-oxygen generation, outcomes that are detrimental for imaging and PDT, so strategies that preserve monomer-like behavior in aqueous media remain a central design goal.[2]

The spectral consequences of aggregation are well rationalized by exciton coupling theory: face-to-face (H-type) stacks exhibit hypsochromically shifted, broadened Q-bands with reduced oscillator strength and quenched emission, whereas head-to-tail (J-type) assemblies red-shift and can enhance 0–0 intensity. These rules of thumb provide practical diagnostics for monitoring Pc aggregation and for screening de-aggregation strategies spectroscopically.[3,4]

Among metals, Zr(IV) is attractive because its high coordination number enforces out-of-plane (axial) ligation, enabling installation of solubilizing or functional ligands without perturbing the Pc π-system directly. We and others have shown that axially substituted Zr(IV) (and Hf(IV)) phthalocyanines have been widely explored; their synthesis, solution behavior, and spectroscopy highlight how axial donors shape aggregation and photophysics.[5,6]

Supramolecular encapsulation with cyclodextrins (CDs) is a particularly effective, formulation-level approach to mitigate Pc aggregation in water. The hydrophobic CD cavity and hydrophilic rims can host Pc peripheries or axial substituents; β-cyclodextrin (β-CD) offers a size match for many aromatics, while 2-hydroxypropyl-β-cyclodextrin (HP-β-CD) improves aqueous compatibility and complex stability. For multiple Pc families, complexation with β-CD/HP-β-CD increases apparent solubility, decreases H-type stacking, and restores fluorescence/photosensitizing activity.[7,8]

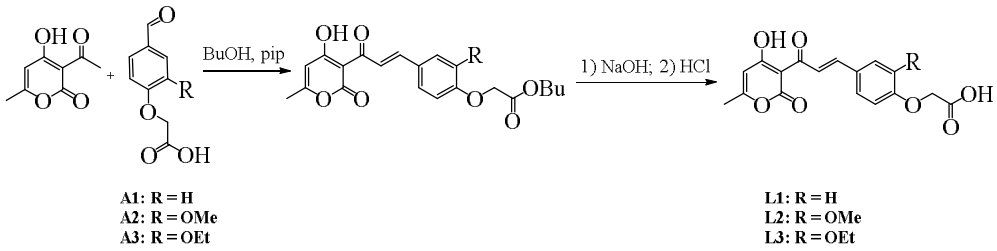
Chalcones are synthetically accessible, π-extended ligands bearing hard donor motifs (e.g., phenolic OH, β-dicarbonyl) that can chelate metals and tune local polarity and hydrogen-bonding around a chromophore. Their coordination chemistry is rich and compatible with high-coordination metals, making them appealing as axial ligands for PcZr(IV) complexes to modulate solubility and aggregation without altering the macrocycle core.[6]

Herein, we describe the synthesis and photophysical characterization of axially ligated zirconium phthalocyanines $PcZr(L)_2$ bearing carboxyl-functionalized chalcone ligands L1–L3. The specific aim was to determine how solvent polarity, aqueous alkalinity, and cyclodextrin additives influence the monomer–aggregate balance and emission response of these complexes. DMSO solutions were used as monomer-like references, whereas aqueous $NaHCO_3$ solutions were used to evaluate aggregation. The

working hypothesis was that suitable cyclodextrins, especially β-CD derivatives, would shift the apparent monomer–aggregate balance toward less aggregated species in water.

Results and Discussion

Carboxyl-functionalized chalcones **L1–L3** were synthesized by Knoevenagel condensation of aldehydes **A1–A3** with dehydroacetic acid, followed by hydrolysis of the corresponding ester intermediates (Scheme 1). Under the reaction conditions, butyl ester intermediates are formed. In the case of **L1**, the butyl ester was isolated in pure form, whereas for **L2** and **L3**, the intermediates were not isolated and were directly subjected to hydrolysis. The structures of the obtained compounds were confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra exhibit characteristic signals corresponding to the –OH proton of the β-ketoenol fragment (17.9 – 17.0 ppm), the –CH proton of the pyran ring (~ 6.3 ppm), the methyl group (~ 2.3 ppm), and other expected signals. The markedly downfield position of the –OH signal indicates the presence of an intramolecular hydrogen bond within the β-ketoenol fragment of the molecules.



Scheme 1. Knoevenagel condensation of aldehydes **A1-A3** with dehydroacetic acid followed by hydrolysis to afford carboxyl-functionalized chalcones **L1-L3**.

We first examined the photophysical behavior of chalcones L1–L3 across organic and aqueous media. Typically, the chalcones are readily soluble in alkaline aqueous media owing to the aliphatic carboxylate and can chelate metal ions, including coordination-unsaturated Zr/Hf phthalocyanines via the 4-OH and 3-acyl groups of the pyran ring. In organic solvents (CH_2Cl_2, $CHCl_3$, DMF, DMSO) the UV-Vis spectra show two partially overlapping bands, whereas in MeOH and 0.05 M aqueous $NaHCO_3$ a single, broader band is observed (Figure 1, S1).

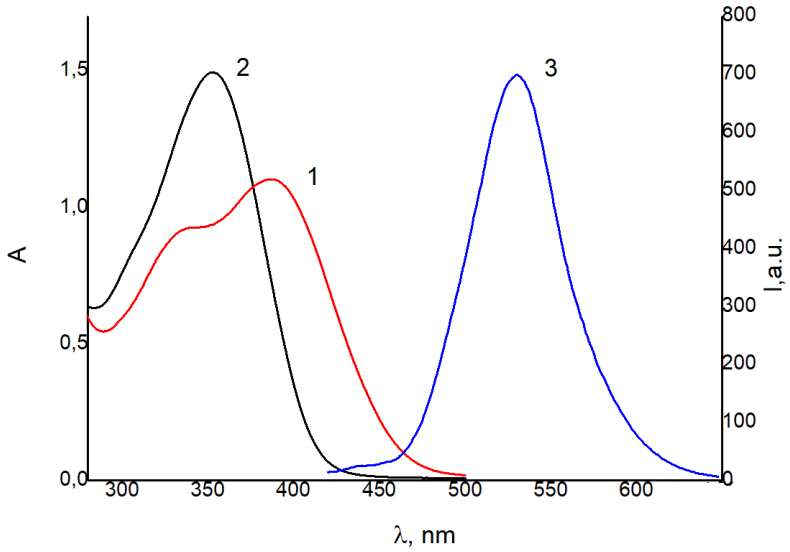


Figure 1. UV-Vis spectra of **L3** in DMSO (1), in 0.05 M aqueous $NaHCO_3$ solution (2) ($C = 1 \times 10^{-4}$ mol/L) and fluorescence emission spectra of L3 in DMSO (3).

To accurately determine the position of the absorption bands, the experimental spectra were deconvoluted into individual Gaussian components. Molar absorption coefficients (ε) were determined using UV-Vis spectrophotometry within the studied concentration range (Table 1).

Table 1. Absorption, excitation, and emission (FL) spectral data of compounds **L1–L3** in various solvents.

	UV-Vis, λ_{max}, nm, ($\varepsilon \cdot 10^{4)}$						FL	
	CH_2Cl_2*	$CHCl_3$*	DMF*	DMSO*	MeOH	0.05 M aqueous $NaHCO_3$ solution	DMSO λ_{ex}, nm	DMSO λ_{em} nm, (I, a.u.)
L1	323(1.0), 379(2.9)	320(0.9), 381(3.1)	324(1.1), 380(1.9)	358(1.7), 389(2.6)	379(3.1)	340(1.8)	385	485(421)
L2	323(1.0), 391(2.0)	322(1.0), 393(2.3)	323(1.2), 387(1.6)	325(0.9), 397(1.9)	385(2.5)	352(1.4)	400	528(954)
L3	328(1.0) 391(2.0)	325(1.0), 393(2.6)	329(1.3), 391(1.8)	329(0.9), 397(1.7)	386(2.7)	352(1.4)	400	530(700)

*λ_{max} values were determined by deconvolution of the spectra into Gaussian components.

Fluorescence from **L1–L3** in DMSO appears between 485 – 530 nm with large Stokes shifts (ca. 100–130 nm; Table 1), whereas emission is strongly quenched in water, which is consistent with increased non-radiative decay in protic/aggregating media.

Because many dyes self-assemble at~~with~~ increasing concentration[11] or in mixtures of organic solvents with water,[12] we assessed Beer–Lambert behavior for **L1–L3** in DMSO and aqueous $NaHCO_3$. Within the concentration range 1.0×10^{-5} – 1.5×10^{-4} M, absorbance varied linearly with concentration in both media (Figure 2, S2). This suggests that the observed spectral differences between DMSO and aqueous $NaHCO_3$ arise primarily from solvent-dependent speciation rather than from progressive concentration-dependent aggregation within the studied range.

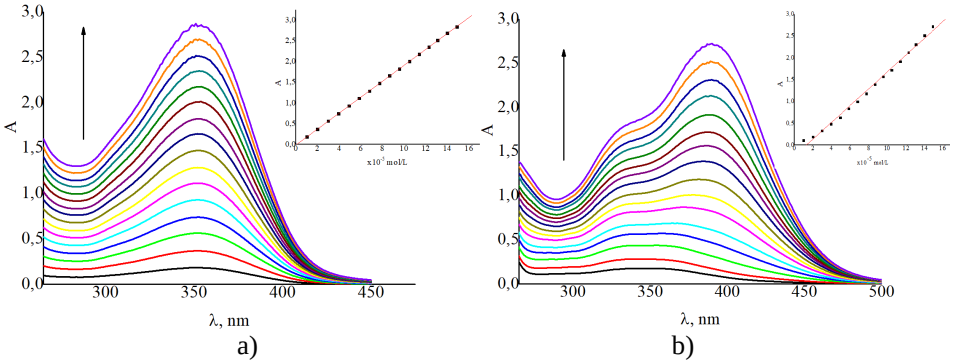
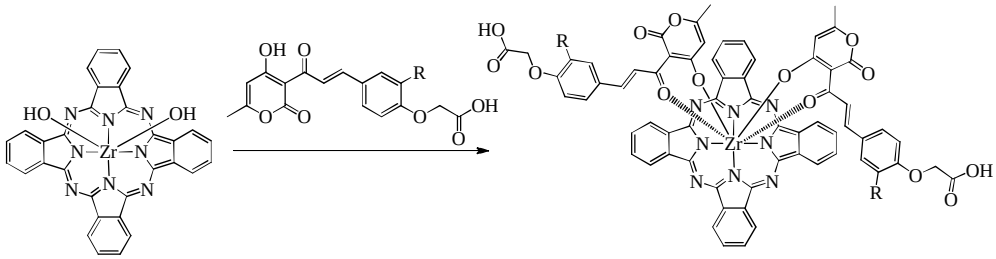


Figure 2. Changes in the UV-Vis absorption spectra of compound **L2** in DMSO (**a**) and in 0.05 M aqueous $NaHCO_3$ solution (**b**) within the concentration range of $1.0 \times 10^{-5} – 1.5 \times 10^{-4}$ mol/L. Insets: plots showing compliance of the solutions with the Beer–Lambert law.

The zirconium phthalocyanine complexes $PcZr(L)_2$ were then synthesized by replacing the axial hydroxo ligands of $PcZr(OH)_2$ with the chalcone ligands L1–L3 under reflux in DMF (Scheme 2).[10] The obtained **$PcZr(L)_2$** complexes are blue crystalline solids soluble in DMSO, MeOH, $CHCl_3$, and alkaline water. The ^1H NMR spectra showed resonances characteristic of the phthalocyanine macrocycle (.7– 8.9 and 8.6 – 7.8 ppm), aromatic ligand protons (7 – 6 ppm), pyran CH (4.9 – 4.6 ppm), and methyl groups (~ 2.0 ppm); integrals are consistent with two out-of-plane ligands coordinated to Zr.



$PcZr(L1)_2$: R = H
$PcZr(L2)_2$: R = OMe
$PcZr(L3)_2$: R = OEt

Scheme 2. Axial ligand substitution of $PcZr(OH)_2$ with carboxyl-functionalized chalcones **L1-L3** to form $PcZr(L)_2$ complexes.

In DMSO, the UV-Vis spectra display the expected Pc features: Soret (330 – 350 nm), Q-band (690 – 695 nm), and additional ligand-centered bands at 390 – 415 nm (Figure 3a, S3). In water/alkaline media, the spectral pattern changes to one typical of aggregated phthalocyanines,[13] the Q-band hypsochromically shifts and decreases in intensity, while a new band near ~ 640 – 644 nm grows (Figure 3b, S3). Together with band broadening, these changes are consistent with the formation of H-type, face-to-face aggregates, which typically show reduced oscillator strength of the monomeric Q transition and quenched emission.[2]

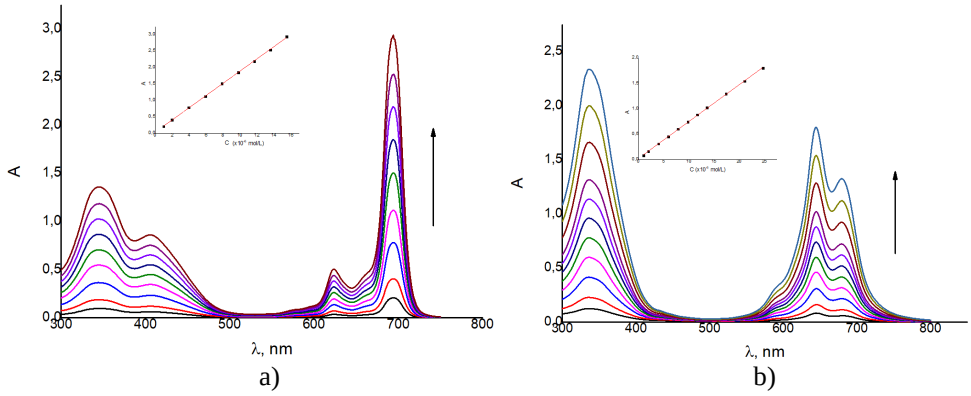
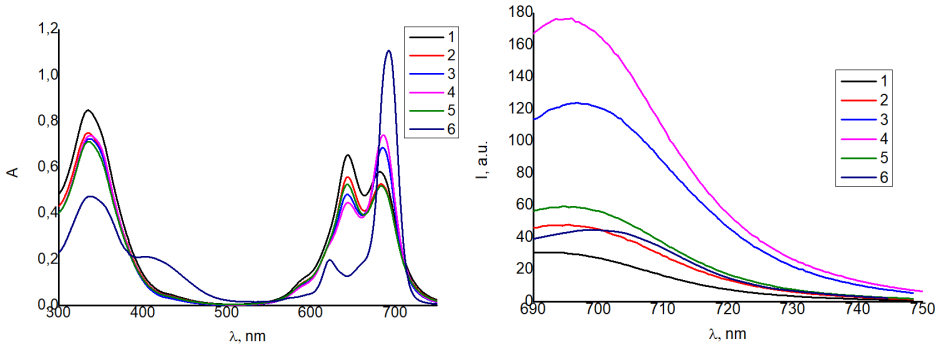


Figure 3. Changes in the UV-Vis spectra of **PcZr(L2)$_2$** in DMSO (**a**) and in 0.05 M aqueous $NaHCO_3$ solution (**b**) over the concentration range from 2×10^{-6} to 1.2×10^{-5} M. Insets: plots demonstrating compliance of the solutions with the Beer–Lambert law.

Beer–Lambert plots for 2.0×10^{-6} to 1.2×10^{-5} M solutions were linear in both DMSO and aqueous $NaHCO_3$ (Figure 3). Therefore, within this concentration interval, the aqueous aggregate/monomer ratio appears not to change substantially with concentration; the dominant change is instead associated with transfer from DMSO to aqueous alkaline medium.

Cyclodextrins are widely used to improve the aqueous compatibility and photophysical behavior of hydrophobic fluorophores.[14] Therefore, we evaluated whether α-CD, β-CD, γ-CD, and HP-β-CD could modify the aggregation state of $PcZr(L)_2$ complexes in aqueous $NaHCO_3$ solution.

Adding α-CD or γ-CD at a 1:10 (Pc:CD) ratio caused minimal spectral changes (Figure 4, S4). In contrast, β-CD and HP-β-CD produced clearer spectral changes consistent with partial recovery of monomer-like character: the Q-band near 680 – 686 nm increased, whereas the aggregate-associated band near 643 – 644 nm decreased (Figure 4a, Table 2).



a) b)

Figure 4. UV-Vis (**a**) and fluorescence spectra (**b**) of **PcZr(L3)$_2$** in 0.05 M aqueous $NaHCO_3$ solution – 1; in aqueous solutions with added cyclodextrins (α-CD – 2; β-CD -3; HP-β-CD – 4; γ-CD – 5) and in DMSO – 6.

Fluorescence excited at 680 nm increased 2 – 3 times relative to additive-free aqueous solutions, with emission maxima 690 – 699 nm and modest Stokes shifts (10 – 19 nm), consistent with Pc emission from less-aggregated species.

The differential efficacy follows the classical cavity-size and hydrophobic microenvironment argument: the β-CD cavity (~6–6.5 Å) better accommodates peripheral ligand motifs and portions of the Pc macrocycle/substituents than α-CD (too small) or γ-CD (too large/less snug). HP-β-CD adds improved solubilization via hydroxypropyl groups, further shifting the monomer–aggregate equilibrium toward monomers. While the data do not delineate the exact stoichiometry, the combined Q-band recovery + fluorescence enhancement strongly supports reduced H-type stacking in β-CD/HP-β-CD media.

Table 2. UV–Vis absorption and fluorescence data for $PcZr(L)_2$ complexes in DMSO and 0.05 M aqueous $NaHCO_3$ solution in the absence and presence of cyclodextrins.

Compound	Solvent	Q band λ_{max}, nm ($\varepsilon \cdot 10^5$ $M^{-1}cm^{-1}$)	Excitation λ_{ex}, nm	Emission λ_{em}, nm ($I_{rel.\ a.u.}$)	Stokes shift $\Delta\lambda$, nm
$PcZr(L1)_2$	DMSO	694(1.50)	680	690	10
$PcZr(L1)_2$	water	643(0.57); 679(0.44)	680	694	14
$PcZr(L1)_2$+α-CD	water	643(0.45); 681(0.36)	680	697(33)	17
$PcZr(L1)_2$+β-CD	water	643(0.42); 684(0.50)	680	699(80)	19
$PcZr(L1)_2$+HP-β-CD	water	644(0.41); 684(0.57)	680	697(163)	17
$PcZr(L1)_2$+γ-CD	water	643(0.47); 681(0.40)	680	697(39)	17
$PcZr(L2)_2$	DMSO	693(1.16)	680	690	10
$PcZr(L2)_2$	water	644(0.40); 680(0.37)	680	695	15
$PcZr(L2)_2$+α-CD	water	644(0.33); 681(0.27)	680	696(54)	16
$PcZr(L2)_2$+β-CD	water	643(0.20); 686(0.40)	680	699(209)	19
$PcZr(L2)_2$+HP-β-CD	water	644(0.20); 685(0.35)	680	697(146)	17
$PcZr(L2)_2$+γ-CD	water	643(0.30); 682(0.29)	680	695(44)	15
$PcZr(L3)_2$	DMSO	693(1.10)	685	699(45)	14
$PcZr(L3)_2$	water	644(0.35); 682(0.30)	680	693(31)	13
$PcZr(L3)_2$+α-CD	water	644(0.30); 683(0.25)	680	695(48)	15
$PcZr(L3)_2$+β-CD	water	643(0.25); 685(0.35)	680	697(124)	17
$PcZr(L3)_2$+HP-β-CD	water	644(0.20); 686(0.35)	680	695(177)	15
$PcZr(L3)_2$+γ-CD	water	643(0.25); 684(0.25)	680	695(59)	15

Cyclodextrin-containing samples were prepared at a Pc:CD molar ratio of 1:10. Fluorescence intensities are given in arbitrary units and should be compared only within measurements recorded under identical instrumental settings.

It should be noted that the present data do not establish the exact stoichiometry or binding constants of the $PcZr(L)_2$-cyclodextrin assemblies. Therefore, the role of cyclodextrins is discussed here in terms of apparent changes in aggregation state inferred from absorption and fluorescence spectra. More detailed host-guest characterization would be required to define the inclusion geometry and binding equilibria.

Experimental

All reagents (Fluka, Aldrich) and solvents were used without further purification. α-, β-, and γ-Cyclodextrins (CDs), as well as 2-hydroxypropyl-β-cyclodextrin (HP-β-CD) (TCI, Tokyo, Japan), were used to prepare stock solutions in water by dissolving 125 mg of the corresponding CD in 5 mL of water. ^{1}H NMR spectra were recorded on a Varian NMR spectrometer operating at 400 MHz for protons, using DMSO-d_6 as the solvent. Tetramethylsilane was used as the internal standard. UV-Vis spectra were recorded using a Shimadzu UV-3600 spectrophotometer in 10×10 mm quartz cuvettes in dichloromethane, chloroform, DMF, DMSO, methanol, and 0.05 M aqueous $NaHCO_3$ solution. Fluorescence spectra were obtained using a Perkin Elmer Fluorescence Luminescence Spectrometer LS 55. Unless otherwise stated, absorption and fluorescence spectra were recorded at room temperature using freshly prepared solutions. For cyclodextrin experiments, aqueous $PcZr(L)_2$ solutions were treated with cyclodextrin additives at a Pc:CD molar ratio of 1:10. Fluorescence spectra of $PcZr(L)_2$ complexes were recorded upon excitation in the Q-band region. Relative fluorescence intensities are reported in arbitrary units and were compared only for spectra measured under identical instrumental settings. Mass spectra were obtained using a Bruker Daltonics ultraflex II MALDI-TOF/TOF mass spectrometer. The starting aldehydes were synthesized by

alkylation of the corresponding hydroxybenzaldehydes with chloroacetic acid under aqueous alkaline conditions.[9]

General procedure for the synthesis of benzaldehydes A1–A3

Aldehydes A1-A3 have been synthesized using previously reported protocol[9]. Thus, a mixture of 0.2 mol of chloroacetic acid and 0.1 mol of the corresponding aldehyde is suspended in 50 mL of cold water. Then, 0.3 mol of concentrated aqueous sodium hydroxide solution is gradually added. Once a homogeneous solution is obtained, the mixture is heated to boiling until the pH approaches neutrality. At this point, additional sodium hydroxide solution is added to adjust the pH to approximately 12. The addition is continued until the pH stabilizes and no longer decreases. The reaction mixture is then cooled and acidified with concentrated hydrochloric acid to a strongly acidic pH. The resulting precipitate is filtered and washed with water until neutral. Aldehyde A1 is recrystallized from water, while aldehydes A2 and A3 are repeatedly boiled with water and filtered hot, discarding the aqueous fraction. The resulting products are dried at 50 °C for 12 hours.

A1. *2-(4-formylphenoxy)acetic acid***.** Yield 12.1 g (67.2%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.96 (s, 1H), 9.87 (s, 1H), 7.86 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 4.83 (s, 2H).

A2. *2-(4-formyl-2-methoxyphenoxy)acetic acid***.** Yield 13.8 g (65.7%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (s, 1H), 9.83 (s, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.41 (s, 1H), 7.05 (d, J = 8.2 Hz, 1H), 4.82 (s, 2H), 3.84 (s, 3H).

A3. *2-(2-ethoxy-4-formylphenoxy)acetic acid***.** Yield 10.2g (45.5%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.06 (s, 1H), 9.81 (s, 1H), 7.48 (d, J =

8.3 Hz, 1H), 7.39 (s, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 4.82 (s, 2H), 4.09 (q, *J* = 6.9 Hz, 2H), 1.34 (t, *J* = 6.9 Hz, 3H).

General procedure for the synthesis of chalcones L1–L3.

Dehydroacetic acid (0.03 mol, 5.04 g) and 0.03 mol of the corresponding aldehyde were dissolved in 50 mL of butanol with heating. After complete dissolution, 5 drops of piperidine (pip) were added, and the reaction mixture was refluxed using a Dean–Stark apparatus for 5 hours. Following this, 10 mL of butanol were distilled off, and the mixture was left in a refrigerator at 5 °C overnight. The resulting precipitate was filtered, washed three times with 10 mL portions of methanol, and dissolved in a slight excess of 5% aqueous sodium hydroxide solution. To the alkaline solution, 0.5 g of activated charcoal was added, stirred for a few minutes, and filtered. In the case of compound **L1**, the butyl ester was isolated in pure form. Its hydrolysis was carried out under more rigorous conditions by heating the alkaline solution to 60 °C. For compounds **L2** and **L3**, the butyl esters were not isolated; instead, the hydrolysis was performed directly in aqueous alkali. The filtrate was acidified with hydrochloric acid to pH 1. The resulting precipitate was filtered off, washed with water until neutral, and dried under vacuum at 60 °C.

L1-butyl ester. *Butyl (E)-2-(4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)phenoxy)acetate.* Yield 6.0 g, (60.6%). ^{1}H NMR (400MHz, DMSO-d_6) δ 13.10 (s, 1H), 8.06 (d, *J* = 15.7 Hz, 1H), 7.90 (d, *J* = 15.7 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.28 (s, 1H), 4.88 (s, 2H), 4.11 (t, *J* = 6.5, 6.5 Hz, 2H), 2.26 (s, 3H), 1.55 (p, *J* = 6.6, 6.6, 6.6, 6.6 Hz, 2H), 1.28 (dq, *J* = 14.6, 7.3, 7.3, 7.3 Hz, 2H), 0.85 (t, *J* = 7.3, 7.3 Hz, 3H).

L1. *(E)-2-(4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)phenoxy)acetic acid.* Yield 4.6 g, (46.4%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 17.87 (s, 1H), 13.14 (s, 1H), 8.08 (d, J = 15.7 Hz, 1H), 7.92 (d, J = 15.7 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.30 (s, 1H), 4.78 (s, 2H), 2.27 (s, 3H).

L2. *(E)-2-(4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)-2-methoxyphenoxy)acetic acid.* Yield 4.3 g, (39.8%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 17.81 (s, 1H), 12.96 (s, 1H), 8.05 (d, J = 15.7 Hz, 1H), 7.90 (d, J = 15.8 Hz, 1H), 7.32 (s, 2H), 6.97 (d, J = 8.9 Hz, 1H), 6.29 (s, 1H), 4.77 (s, 2H), 3.85 (s, 3H), 2.27 (s, 3H).

L3. *(E)-2-(2-ethoxy-4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)phenoxy)acetic acid.* Yield 1.6 g, (14.3%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 16.95 (s, 1H), 13.07 (s, 1H), 8.03 (d, J = 15.4 Hz, 1H), 7.88 (d, J = 15.4 Hz, 1H), 7.30 (s, 2H), 6.94 (m, 1H), 6.28 (s, 1H), 4.78 (s, 2H), 4.10 (m, 2H), 2.26 (s, 3H), 1.36 (t, 3H).

Synthesis of zirconium phthalocyanine complexes with chalcones as out-of-plane ligands (PcZr(L)$_2$). $PcZr(OH)_2$ (0.25 mmol, 159.5 mg), prepared according to,[10] and 0.55 mmol (10% excess) of the corresponding chalcone were placed in a flask and dissolved in 4 mL of DMF. The mixture was refluxed under an inert atmosphere with stirring for 3 hours. The hot reaction mixture was filtered, and the filtrate was stored in a refrigerator for 18–24 hours. The resulting crystals were filtered, washed with 3 mL of acetonitrile, and dried under vacuum at 60 °C.

PcZr(L1)$_2$. *Bis-[(E)-2-(4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)phenoxy)acetato] zirconium phthalocyaninate*. Yield 155 mg (49%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 – 8.97 (m, 8H), 8.58 – 8.09 (m, 8H), 6.97 (d, J = 14.1 Hz, 2H), 6.93 – 6.73 (m, 8H),

6.28 (d, *J*=15.1 Hz, 2H), 5.12 – 4.59 (m, 2H), 3.59 (s, 4H), 2.07 (s, 6H). MS (MALDI-TOF positive mode): m/z 1261.1919 (calcd. for $[M+H]^+$ - $[C_{66}H_{42}N_8O_{14}Zr+H]^+$ 1261.1941); 931.1248 (calcd. for $[PcZrL]^+$ - $[C_{49}H_{29}N_8O_7Zr]^+$ 931.1206); 619.0742 (calcd. for $[PcZr=O+H]^+$ - $[C_{32}H_{16}N_8OZr+H]^+$ 619.0567).

PcZr(L2)$_2$. *Bis-[(E)-2-(4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)-2-methoxyphenoxy)acetato] zirconium phthalocyaninate*. Yield 135 mg (41%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 – 8.86 (m, 8H), 8.56 – 7.77 (m, 8H), 6.94 (d, *J* = 14.9 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.62 (s, 2H), 6.43 – 6.16 (m, 4H), 4.92 (s, 2H), 4.72 (s, 4H), 3.66 (s, 6H), 2.05 (s, 6H). MS (MALDI-TOF positive mode): m/z 1320.2510 (calcd. for $[M]^+$ - $[C_{68}H_{46}N_8O_{16}Zr]^+$ 1320.2079); 961.1649 (calcd. for $[PcZrL]^+$ - $[C_{50}H_{31}N_8O_8Zr]^+$ 961.1312); 619.0811 (calcd. for $[PcZr=O+H]^+$ - $[C_{32}H_{16}N_8OZr+H]^+$ 619.0567).

PcZr(L3)$_2$. *Bis-[(E)-2-(2-ethoxy-4-(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxoprop-1-en-1-yl)phenoxy) acetato] zirconium phthalocyaninate*. Yield 211 mg (62%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 – 9.08 (m, 8H), 8.59 – 8.09 (m, 8H), 7.06 – 6.80 (m, 4H), 6.69 (s, 2H), 6.36 – 5.97 (m, 4H), 4.92 (s, 2H), 4.01 – 3.81 (m, 4H), 2.72 – 2.53 (m, 4H), 2.19 – 1.90 (m, 6H), 1.57 (s, 6H). MS (MALDI-TOF positive mode): m/z 1349.3096 (calcd. for $[M+H]^+$ - $[C_{70}H_{50}N_8O_{16}Zr+H]^+$ 1349.2465); 975.1685 (calcd. for $[PcZrL]^+$ - $[C_{51}H_{33}N_8O_8Zr]^+$ 975.1468); 619.0759 (calcd. for $[PcZr=O+H]^+$ - $[C_{32}H_{16}N_8OZr+H]^+$ 619.0567).

Conclusions

Carboxyl-functionalized chalcones **L1–L3** and their axially ligated zirconium phthalocyanine complexes $PcZr(L)_2$ were synthesized and characterized by spectroscopic methods. The chalcones displayed solvent-

dependent absorption and fluorescence behavior, with pronounced emission in DMSO and weak emission in aqueous medium. For the $PcZr(L)_2$ complexes, DMSO solutions showed monomer-like Soret and Q-band features, whereas aqueous $NaHCO_3$ solutions showed hypsochromically shifted and broadened Q-bands with reduced fluorescence, consistent with H-type aggregation.

Within the investigated concentration ranges, the absorption spectra followed Beer–Lambert behavior, suggesting that the main spectral changes are associated with solvent-dependent speciation rather than progressive concentration-dependent aggregation. Addition of β-CD and HP-β-CD partially restored monomer-like absorption features and enhanced fluorescence in aqueous medium, whereas α-CD and γ-CD were less effective. These observations indicate that cyclodextrin-based formulation, especially using β-CD or HP-β-CD, is a simple non-covalent strategy for improving the aqueous photophysical response of axially substituted $PcZr(L)_2$ complexes.

Acknowledgements

This work has received funding from the H2020-MSCA-RISE-2019 under grant agreement No 872331 (acronym: NoBiasFluors).

Conflicts of interest

The authors declare that they have no conflicts of interest.

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