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## **Supplementary Material**

The role of the solvent and concentration on the properties of oxime bearing A<sub>2</sub>B corroles

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## **1. Experimental Details**

## 1.1. Materials

Chemicals were purchased from commercial suppliers and used without further purification, unless described otherwise. For the photophysical studies, all the solutions were prepared with solvents of spectroscopic grade from Uvasol – Merck. The model corrole (5,10,15-(triphenyl)corrole) was purchase from PorphyChem.

**1.2. General Information:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker Avance III instrument operating at 400 and 100 MHz, respectively. The solvents were hexadeuterodimethyl sulfoxide (DMSO- $d_6$ ) and octadeuterotetrahydrofuran (THF- $d_8$ ), as indicated in each case. Chemical shifts are expressed in ppm relative to TMS and coupling constants (*J*) are in Hz. Multiplicity was abbreviated as follows: s: singlet, m: multiplet, br s: broad singlet, br d: broad duplet. High-resolution mass spectra (HMRS) were obtained with a TOF VG Autospect M spectrometer with electrospray ionization (ESI). Thin-layer chromatography (TLC) analyses were performed using precoated silica gel plates Macherey-Nagel Xtra SIL G/UV254. Flash column chromatography was performed with silica gel 60 (0.035–0.070 mm) provided by Acros Organics, as the stationary phase. 1,1-Dichloro-2-acetophenone oxime,<sup>1</sup> 5-phenyldipyrromethane<sup>2</sup> and 5,15-diphenyl-10-(1-hydroxyiminomethyl)corrole (Me-H)<sup>3</sup> were prepared as described in the literature, and 5,10,15-(triphenyl)corrole (model) was purchased from PorphyChem SAS (www.porphychem.com).

#### 1.3. Synthesis and structural characterization of Ph-H corrole

*trans*-A<sub>2</sub>B-Corroles containing an oxime functionality were obtained following a previosly developed general synthetic methodology.<sup>3</sup> The synthesis and characterization of Me-H corrole was previously described.<sup>3</sup> Ph-H corrole was prepared as described below. The <sup>1</sup>H NMR and <sup>13</sup>C NMR are presented at Fig. SI1 and SI2.

(*E*)- and (*Z*)-5,15-Diphenyl-10-[1-hydroxyimino-1-(phenyl)methyl]bilanes: 5-Phenyldipyrromethane (4 mmol, 0.888 g) and a solution of 1,1-dichloro-2-acetophenone oxime (1 mmol, 0.204 g) in dichloromethane (2.4 mL) were added to a solution of Na<sub>2</sub>CO<sub>3</sub> (10 mmol, 1.06 g) in water (14.6 mL). The reaction mixture was stirred at room temperature for 20 min. After this time, the mixture was extracted with ethyl acetate (3 × 20 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The products were purified by flash chromatography [ethyl acetate/hexane (1:2)] giving bilanes (0.168 g, 28%) as a mixture of isomers E:Z (41:59) as a beige solid.

Data for (*Z*)-isomer: <sup>1</sup>H NMR δ (DMSO-*d*<sub>6</sub>) 5.13 (s, 1H), 5.28-5.30 (m, 2H), 5.46-5.54 (m, 4H), 5.65 (br s, 2H), 5.87-5.90 (m, 2H), 6.57-6.60 (s, 2H), 7.04-7.31 (m, 15H), 10.37-10.46 (m, 4H), 10.62 (s, 1H).

Data for (*E*)-isomer: <sup>1</sup>H NMR δ (DMSO-*d*<sub>6</sub>) 5.28-5.30 (m, 2H), 5.46-5.54 (m, 4H), 5.58 (br s, 1H), 5.62 (br s, 1H), 5.84-5.86 (m, 2H), 6.13 (s, 1H), 6.57-6.60 (m, 2H), 7.04-7.31 (m, 15H), 10.52 (br s, 2H), 10.62 (br s, 2H), 11.32 (s, 1H).

HRMS (ESI-TOF) *m/z*: [M+H<sup>+</sup>] Calcd. for C<sub>38</sub>H<sub>33</sub>N<sub>5</sub>O 576.2758; found 576.2764.

5,15-Diphenyl-10-[1-hydroxyimino-1-(phenyl)methyl]corrole (Ph-H): 2,3-Dichloro-5,6dicyano-1,4-benzoquinone (0.72 mmol, 0.163 g) was added to a solution of the (*E*)- and (*Z*)-5,15-diphenyl-10-[1-hydroxyimino-1-(phenyl)methyl]bilanes (0.24 mmol, 0.138 g) in dry tetrahydrofuran (50 mL). The reaction mixture was stirred at room temperature for 3 h. After that time, the reaction mixture was concentrated under reduced pressure until half volume. The product was purified by flash chromatography [ethyl acetate/hexane (1:3)] followed by recrystallization in methanol to give corrole Ph-H (38 mg, 27%) as a dark green solid.

<sup>1</sup>H NMR  $\delta$  (THF-*d*<sub>6</sub>) -2.84 (br s, 2H), -1.09 (br s, 1H), 7.19-7.26 (m, 4H), 7.67-7.80 (m, 8 H), 8.33 (br s, 5H), 8.60 (br d, *J* = 3.6 Hz, 2H), 8.74 (br s, 2H), 8.87 (br s, 2H), 10.53 (br s, 1H); <sup>13</sup>C NMR  $\delta$  (THF-*d*<sub>6</sub>) 98.6, 112.2, 112.7, 112.9, 123.1, 123.3, 125.2, 125.3, 125.9, 126.2, 128.6, 133.0, 138.4, 138.9, 154.8; HRMS (ESI-TOF) *m/z*: [M+H<sup>+</sup>] Calcd. for C<sub>38</sub>H<sub>27</sub>N<sub>5</sub>O 570.2288; found 570.2290;

## 1.4. Photophysical Characterization

## 1.4.1. Sample preparation

An appropriate amount of powder of each compound was weighted to produce a stock solution of  $\sim 10^{-4}$  mol L<sup>-1</sup> when diluted in 5.0 mL of spectroscopic grade solvent. Then, an aliquot of the stock solution was diluted with the proper amount of solvent to obtain the desired concentration in 3.0 mL of final volume. The stock solutions were kept in the dark and prepared immediately prior to use.

## 1.4.2. Determination of nonaqueous pK values of corroles

Equilibrium constants (log *K*) of the protonation and deprotonation reactions of the corroles were determined spectrophotometrically, with the addition of either trifluoroacetic acid (TFA, pKa = 0.23)<sup>4</sup> or 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, pK<sub>aH</sub> = 16.9 in THF),<sup>5</sup> respectively, to a corrole solution. The Hill equation,<sup>6</sup>which analyzes changes in UV-visible spectra during the titration as a function of the concentration of added acid or base to the corrole solution, was used to calculate the equilibrium constant (log *K*) which enabled calculation of relative p*K* values for all the corroles under study.<sup>4, 6</sup>

#### 1.4.3. Steady state and time-resolved fluorescence measurements

The absorption spectra were recorded using Shimadzu UV-2450. Fluorescence spectroscopic studies were performed using Horiba-Jobin-Yvon Fluorolog 3-22 spectrofluorimeter. The fluorescence quantum yields ( $\phi_F$ ) of all compounds in solution were measured using the absolute method with a Hamamatsu Quantaurus QY absolute photoluminescence quantum yield spectrometer, model C11347 (integration sphere).

Fluorescence decays were measured using a home-built Time-Correlated Single Photon Counting (TCSPC) apparatus, as described previously,<sup>7</sup> using an IBH nanoLED (460 nm, 1.0 kHz) as excitation source. The fluorescence decays and the instrumental response function (IRF) were collected using 1024 channels in a time scale up to 97.1 ps/channel; alternate measurements (500 counts) of the pulse profile at the excitation wavelength and the sample emission were performed until 3000 counts at the maximum were reached. All the samples were prepared immediately before the fluorescence decay acquisition and deaerated with nitrogen for 20 min to avoid oxygen quenching. Deconvolution of the fluorescence decay curves was performed using modulation function method in the SAND program, as previously reported in the literature.<sup>8</sup>

#### 1.4.4. Theoretical studies

All theoretical calculations were of the density functional theory (DFT) type and carried out using GAMESS-US version R3.<sup>9</sup> A range corrected LC-BPBE ( $\omega = 0.20 \text{ au}^{-1}$ ) functional, as implemented in GAMESS-US,<sup>9</sup>was used in both ground- and excited-state calculations. TDDFT calculations, with similar functionals, were used to probe the excited-state potential energy surface (PES). A solvent was included using the polarizable continuum model with the solvation model density to add corrections for cavitation, dispersion, and solvent structure. In TDDFT calculation of Franck-Condon excitations, the dielectric constant of the solvent was split into a "bulk" component and a fast component, which is essentially the square of the refractive index. Under "adiabatic" conditions, only the static dielectric constant was used. DFT and TDDFT calculations, for location of critical points, was carried out using SBKJC ECPs (Stevens-Bash-Krauss-Jasien-Cundari Effective Core Potentials for non-valence electrons with a split-31G for valence electrons).<sup>10-12</sup> The results obtained with the LC-BPBE(20) functional are essentially unscaled raw data from calculations; for the  $S_0 \rightarrow S_n$  transitions, a small correction, which result in the subtraction of 0.05 eV, to account for the difference between zero point and the first vibronic level, was considered. For the resulting optimized geometries time-dependent DFT calculations (using the same functional and basis set as those in the previously calculations) were performed to predict the vertical electronic excitation energies. Molecular orbital contours were plotted using ChemCraft 1.7 program. Frequency analysis for each compound were also computed and did not yield any imaginary frequencies, indicating that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Ground state optimized geometry structures, relevant HOMO and LUMO energy levels, together with the electronic transitions (obtained by time dependent DFT, TDDFT) were calculated with the same level of theory, DFT//LC-BPBE ( $\omega$ =0.2)/SBKJC, and compared to the experimental data. Frequency analyses for each compound were also computed and no imaginary frequencies were observed, thus indicating that the structure of each molecules corresponds to, at least, a local minimum on the potential energy surface.



## 2. NMR characterization of corroles

Fig. SI1. <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR of the (E:Z) mixture of bilanes (DMSO-d<sub>6</sub>).



Fig. SI2. <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR of the corrole Ph-H (400 MHz, THF- $d_8$ ).

# 3. Electronic Spectroscopy data



**Fig. SI3**. Comparison of the normalized absorption and emission spectra of the three corroles in 2methyltetrahydrofuran (2-meTHF) at 298 K and 77 K.



**Fig. SI4**. Absorption spectra of the model corrole in (A) THF, (B) ACN and (C) DMSO in the concentration range from  $0.5 - 50 \times 10^{-6}$  mol L<sup>-1</sup>. Inset: detailed absorption.



Fig. SI5. Determination of molar extinction coefficients ( $\epsilon$ ) of the Model corrole in THF.



Fig. SI6. Determination of molar extinction coefficients ( $\epsilon$ ) of the Model corrole in ACN.



Fig. SI7. Determination of molar extinction coefficients ( $\epsilon$ ) of the Model corrole in DMSO.



**Fig. SI8**. Absorption spectra of Ph-H in (A) THF, (B) ACN and (C) DMSO in the concentration range from  $0.5-50 \times 10^{-6}$  mol L<sup>-1</sup>.



Fig. SI9. Determination of molar extinction coefficients ( $\epsilon$ ) of Ph-H in THF.



Fig. SI10. Determination of the molar extinction coefficients ( $\epsilon$ ) of Ph-H in ACN.



Fig. SI11. Determination of the molar extinction coefficients ( $\epsilon$ ) of Ph-H in DMSO.



**Fig. SI12**. Absorption spectra of Me-H in (A) THF, (B) ACN and (C) DMSO in the concentration range from  $0.5-50 \times 10^{-6}$  mol L<sup>-1</sup>.



Fig. SI13. Determination of the molar extinction coefficients ( $\epsilon$ ) of Me-H in THF.



Fig. SI14. Determination of the molar extinction coefficients ( $\epsilon$ ) of Me-H in ACN.



Fig. SI15. Determination of the molar extinction coefficients ( $\epsilon$ ) of Me-H in DMSO.



Fig. SI16. Comparison of the absorption spectra of corroles in acetonitrile at different concentrations:  $1.0 \times 10^{-6}$  mol L<sup>-1</sup> (pink) and  $30 \times 10^{-6}$  mol L<sup>-1</sup> (green).

Corrole	Concentration (mol L <sup>-1</sup> )	φ <sub>F</sub> <sup>298K</sup>
	1.0×10 <sup>-6</sup>	0.12
Model	5.0×10 <sup>-6</sup>	0.12
	10×10 <sup>-6</sup>	0.11
	1.0×10 <sup>-6</sup>	0.13
Ph-H	5.0×10 <sup>-6</sup>	0.12
	10×10 <sup>-6</sup>	0.10
	1.0×10 <sup>-6</sup>	0.049
MeH	5.0×10 <sup>-6</sup>	0.047
	10×10 <sup>-6</sup>	0.044



Fig. SI17. UV-Vis spectra of model compound, Ph-H and Me-H in ACN with time.

# 4. Spectrophotometric Titrations

## Mathematical equations for the correlation of $K_{tit}$ and $K_a$ (Corrole + DBU)

 $H_3Corr(T2) + DBU \rightarrow H_2Corr K_{tit(n=1)}$ 

$$K_{tit(n=1)} = K_a(H_3Corr (T2))/K_{aH}(DBU)$$
Eq.S11 $logK_{tit(n=1)} = log(K(H_3Corr)/K_{aH}(DBU))$ Eq.S12 $logK_{tit(n=1)} = logK(H_3Corr) - logK_{aH}(DBU)$ Eq.S13 $logK_{tit(n=1)} + logK_{aH}(DBU) = logK_a(H_3Corr)$ Eq.S14 $-logK_{tit(n=1)} - logK_{aH}(DBU) = -logK_a(H_3Corr)$ Eq.S15 $- logK_{aH}(DBU) - logK_{tit} = -logK(H_3Corr)$ Eq.S16 $pK_{aH}(DBU) - logK_{tit} = pK(H_3Corr(T2))$ Eq.S17 $H_3Corr(T1) + H_3Corr(T2) + 2DBU \rightarrow H_2Corr K_{tit(n=2)}$ Eq.S18 $Or (1) + (2)$ (1)  $H_3Corr(T2) + DBU \rightarrow H_2Corr K_{tit(n=1)}(T2)$ Eq.S19 $(2) H_3Corr(T1) + DBU \rightarrow H_2Corr K_{tit}(T1)$ Eq.S110

$$\begin{aligned} K_{tit(n=2)} &= K_{tit(n=1)}(T2) * K_{tit}(T1) & \text{Eq.SI11} \\ \log K_{tit(n=2)} &= \log(K_{tit(n=1)}(T2) * K_{tit}(T1)) & \text{Eq.SI12} \\ \log K_{tit(n=2)} &= \log(K_{tit(n=1)}(T2) + \log K_{tit}(T1)) & \text{Eq.SI13} \\ \log K_{tit(n=2)} - \log(K_{tit(n=1)}(T2) = \log K_{tit}(T1)) & \text{Eq.SI14} \\ \end{aligned}$$
From here when using DBU

$$pK_{aH}(DBU) - \log K_{tit}(T1) = pK(H_3Corr(T1))$$
Eq.SI15

#### when adding TFA

Mathematical equations for the correlation of  $K_{\mbox{\tiny tit}}$  and  $K_{\mbox{\tiny aH}}$ 

Eq.SI16

 $H_3Corr(T2) + TFA \rightarrow H_4Corr^+ K_{tit(n=1)}$  Eq.SI17

 $H_3Corr(T1) + TFA \rightarrow H_4Corr^+ K_{tit}(T1)$  Eq.SI18

$H_3Corr(T2) + H_3Corr(T1) + TFA \rightarrow H_4Corr^+ K_{tit(n=2)}$	Eq.SI19
$K_{tit (n=2)} = K_{tit}(T1) * K_{tit (n=1)}$	Eq.SI20
$\log K_{tit (n=2)} = \log (K_{tit}(T1) * K_{tit(n=1)})$	Eq.SI21
$\log K_{\text{tit}(n=2)} = \log K_{\text{tit}}(T1) + \log K_{\text{tit}(n=1)}$	Eq.SI22
$K_{tit}(T1) = \log K_{tit(n=2)} - \log K_{tit(n=1)}$	Eq.SI23
For any K <sub>tit</sub> ,	
$K_{tit} = K_a(TFA)/K_{aH}(H_4Corr^+)$	Eq.SI24
$\log K_{tit} = \log(K_a(TFA)/K_{aH}(H_4Corr^+))$	Eq.SI25
$\log K_{tit} = \log K_a(TFA) - \log K_{aH}(H_4Corr^+)$	Eq.SI26
$\log K_{tit} - \log K_a(TFA) = -\log K_{aH}(H_4Corr^+)$	Eq.SI27
$\log K_{tit} + pK_a(TFA) = pK_{aH}(H_4Corr^+)$	Eq.SI28



**Fig. SI18.** Comparison of the spectrophotometric titrations of the studied corroles in DMSO with TFA (left) and then DBU (right), along with and the respective corrole spectrum in THF: (A) and (B) model, (C) and (D) Ph-H and (E) and (F) Me-H. [Corrole] =  $5.0 \times 10^{-6}$  mol L<sup>-1</sup>.



**Fig. SI19.** Hill equation fit at 417 nm of the spectrophotometric titrations of corroles in DMSO with TFA (A) model corrole and (B) Ph-H. [Corrole] =  $5.0 \times 10^{-6}$  mol L<sup>-1</sup>.



**Fig. SI20**. Titration of corroles in ACN with increasing TFA concentration. (A) Model corrole; (B) Ph-H and (C) Me-H. Inset: Hill equation fit at 575 nm, for n = 1. [Corrole] =  $5.0 \times 10^{-6}$  mol L<sup>-1</sup>.



Fig. SI21. Influence of DBU addition on the absorption (A) and emission (B) spectra of Me-H in THF. Experimental conditions: [Corrole] =  $5.0 \times 10^{-6}$  mol L<sup>-1</sup>, emission spectra were acquired with  $\lambda^{ex} = 527$  nm, with absorption values from 0.0357 (THF) to 0.0277 (THF + 4 eq DBU) at the excitation wavelength.

# 5. TDDFT data

**Table SI2.** Absorption maximum experimental (Exp.) and theoretical (Calc.) values and major contribution for the transition (Trans.), in different solvents, for corrole model compound. The oscillator force (*f*) and the respective electronic transition (Trans.) are reported together with the data obtained at the level theory of the DFT//LC-BPBE( $\omega$ =0.2)/SBKJC.

Solvent	Exp.		Calc. ( <i>f</i> )	Trans.
		T1	282 (0.115)	HOMO-10 → LUMO (55%)
			385 (1.542)	HOMO-1 $\rightarrow$ LUMO+1 (90%)
			416 (1.332)	HOMO → LUMO+1
			616 (0.409)	(74%)
THF	281/416/572/616/653			HOMO $\rightarrow$ LUMO (91%)
	2011 110/372/010/033	T2 F 282 (0.039)	$\begin{array}{c} \text{HOMO-12} \rightarrow \text{LUMO} \\ (41\%) \end{array}$	
			378 (1.344)	HOMO-1 $\rightarrow$ LUMO+1 (90%)
			410 (1.347)	HOMO → LUMO+1
			603 (0.509)	(74%)
				HOMO → LUMO (93%)
		T1	288 (0.085)	HOMO-3 $\rightarrow$ LUMO (43%)
			288 (0.083) 383 (1.521)	HOMO-1 $\rightarrow$ LUMO+1 (90%)
			412 (1.296)	HOMO → LUMO+1
			615 (0.396)	(74%)
				HOMO → LUMO (91%)
ACN	289/415/518/633	T2	280 (0.000)	HOMO-10 → LUMO (55%)
			269(0.099) 376(1.330)	HOMO-1 → LUMO+1
			370(1.330)	(90%)
			407 (1.313) 602 (0.488)	HOMO $\rightarrow$ LUMO+1 (74%)
			002 (0.400)	$HOMO \rightarrow LUMO (93\%)$
		H <sub>2</sub> Corr-	384 (1.278)	HOMO-1 $\rightarrow$ LUMO+1 (91%)

			420 (1.263) 621 (0.457)	HOMO $\rightarrow$ LUMO+1 (75%)
				HOMO → LUMO (94%)
		Homoconjugated Complex	404 (1.798)	HOMO-1 → LUMO+1 (59%)
		(corrole dimer)	419 (0.951)	HOMO $\rightarrow$ LUMO+1
			631 (0.392)	(80%)
				HOMO → LUMO (82%)
				HOMO-3 → LUMO (67%)
			325 (0.05)	HOMO-1 → LUMO+1
		H <sub>2</sub> Corr	386 (1.302)	(92%)
DMSO	324/427/448/542/593/642		424 (1.306)	HOMO $\rightarrow$ LUMO+1
			544 (0.007)	(/6%)
			624 (0.480)	HOMO-1 → LUMO (75%)
				HOMO → LUMO (94%)



**Fig. SI22.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for the model corrole in THF and representative optimized geometry.



**Fig. SI23.** Orbital contours of the HOMO and LUMO for the model corrole – tautomer 2 (T2), in THF.



**Fig. SI24.** Orbital contours of the HOMO and LUMO for the model corrole – tautomer 1 (T1), in THF.



**Fig. SI25.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for the model corrole in DMSO, and representative optimized geometry.



Fig. SI26. Orbital contours of the HOMO and LUMO for model corrole – deprotonated ( $H_2COO^-$ ), in DMSO.



**Fig. SI27.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for the model corrole in acetonitrile, for the model corrole.



**Fig. SI28.** Orbital contours of the HOMO and LUMO for model corrole – "dimer" (aggregate), in acetonitrile.

**Table SI3.** Absorption maximum experimental (Exp.) and theoretical (Calc.) values and major contribution for the transition (Trans.), in different solvents, for oxime-corrole compounds **Ph-H**. The oscillator force (*f*) and the respective electronic transition (Trans.) are reported together with the data obtained at the level theory of the DFT//LC-BPBE( $\omega$ =0.2)/SBKJC.

Solvent	_			_
	Exp.		Calc. ( <i>f</i> )	Trans.
			586 (0.2686)	HOMO → LUMO (89%)
		T1	410 (1.3297)	HOMO $\rightarrow$ LUMO+1 (76%)
			388 (1.4769)	HOMO-1 → LUMO+1 (88%)
THE	202/115/578/600/616		295 (0.0764)	HOMO-2 → LUMO (57%)
ІПГ	302/413/3/8/009/040		571 (0.351)	HOMO-3 → LUMO (91%)
		T2	406 (1.332)	HOMO-3 → LUMO+1 (76%)
			383 (1.291)	HOMO $\rightarrow$ LUMO+1 (88%)
			295 (0.016)	HOMO → LUMO (57%)
			601 (0.321)	HOMO → LUMO (89%)
		T1	529 (0.011)	HOMO-1 → LUMO (73%)
	421/518/579/625		415 (1.274)	HOMO $\rightarrow$ LUMO+1 (73%)
			389 (1.489)	HOMO-1 → LUMO+1 (88%)
			586 (0.410)	HOMO → LUMO (91%)
			532 (0.008)	HOMO-1 → LUMO (73%)
		T2	411 (1.256)	HOMO $\rightarrow$ LUMO+1 (73%)
			385 (1.289)	HOMO-1 → LUMO+1 (88%)
			601 (0.369)	HOMO → LUMO (92%)
ACN		H <sub>2</sub> Corr-	538 (0.002)	HOMO-1 → LUMO (72%)
			431 (1.095)	HOMO $\rightarrow$ LUMO+1 (71%)
			396 (1.165)	HOMO-1 → LUMO+1 (90%)
			619 (0.236)	HOMO-1 → LUMO (72%)
			572 (0.039)	HOMO $\rightarrow$ LUMO+2 (61%)
		Homoconjugated	510 (0.002)	HOMO-1 → LUMO+2 (74%)
		Complex (corrole dimer)	422 (0.173)	HOMO-2 → LUMO+3 (75%)
		```	406 (1.556)	HOMO-1 → LUMO+3 (62%)
			380 (2.103)	HOMO-3 → LUMO+3 (87%)
DMSO	429/445/548/589/634		604 (0.3905)	HOMO → LUMO (92%)

	539 (0.0034)	HOMO-1 → LUMO (73%)
H <sub>2</sub> Cor	r 433 (1.1445)	HOMO $\rightarrow$ LUMO+1 (73%)
	398 (1.1904)	HOMO-1 $\rightarrow$ LUMO+1 (90%)



**Fig. SI29.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for Ph-H in THF.



Fig. SI30. Orbital contours of the HOMO and LUMO for Ph-H – tautomer 1 (T1), in THF.



Fig. SI31. Orbital contours of the HOMO and LUMO for Ph-H – tautomer 2 (T2), in THF.



**Fig. SI32.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for Ph-H in DMSO.



Fig. SI33. Orbital contours of the HOMO and LUMO for Ph-H – deprotonated ( $H_2Corr^-$ ), in DMSO.



Fig. SI34. UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for Ph-H, in acetonitrile.



Fig. SI35. Orbital contours of the HOMO and LUMO for Ph-H – "dimer" (aggregate), in acetonitrile.

**Table SI4.** Absorption maximum experimental (Exp.) and theoretical (Calc.) values, in different solvents, for oxime-corrole compound Me-H. The oscillator force (*f*) and the respective electronic transition (Trans.) are reported together with the data obtained at the level theory of the DFT//LC-BPBE( $\omega$ =0.2)/SBKJC.

Exp.		Calc. ( <i>f</i> )	Trans.
	T1	608 (0.372)	HOMO → LUMO (90%)
		532 (0.015)	HOMO-1 → LUMO (74%)
		413 (1.199)	HOMO → LUMO+1 (74%)
298/415/576/612/646		388 (1.558)	HOMO-1 → LUMO+1 (89%)
		296 (0.004)	HOMO $\rightarrow$ LUMO+3 (78%)
	T2	594 (0.476)	HOMO → LUMO (92%)
		537 (0.014)	HOMO-1 → LUMO (74%)
	Exp. 298/415/576/612/646	Exp. T1 298/415/576/612/646 T2	Exp.         Calc. (f)           T1         608 (0.372)           532 (0.015)         532 (0.015)           413 (1.199)         413 (1.199)           298/415/576/612/646         388 (1.558)           296 (0.004)         296 (0.004)           T2         594 (0.476)           537 (0.014)         537 (0.014)

			408 (1.179)	HOMO $\rightarrow$ LUMO+1 (74%)
			381 (1.370)	HOMO-1 $\rightarrow$ LUMO+1 (89%)
			298 (0.025)	HOMO-3 → LUMO (55%)
		T1		HOMO $\rightarrow$ LUMO (90%)
			606 (0.357)	HOMO-1 $\rightarrow$ LUMO (74%)
			531 (0.014)	HOMO $\rightarrow$ LUMO+1 (74%)
			410 (1.166)	HOMO-1 $\rightarrow$ LUMO+1
			386 (1.539)	(89%)
		T2	592 (0.451)	HOMO → LUMO (92%)
			536 (0.012)	HOMO-1 → LUMO (73%)
			405 (1.152)	HOMO → LUMO+1 (74%)
	421/437/539/580/628	H <sub>2</sub> Corr—	380 (1.355)	HOMO-1 → LUMO+1 (89%)
			607 (0.420)	HOMO → LUMO (93%)
ACN			538 (0.012)	HOMO-1 → LUMO (75%)
ACI			417 (1.086)	HOMO $\rightarrow$ LUMO+1 (75%)
			387 (1.293)	HOMO-1 $\rightarrow$ LUMO+1 (91%)
				HOMO-1 → LUMO (77%)
		Homoconjugated Complex (corrole dimer)	626 (0.269)	HOMO → LUMO+2 (58%)
			573 (0.044)	HOMO-1 $\rightarrow$ LUMO+1 (87%)
			542 (0.003)	HOMO-3 $\rightarrow$ LUMO+2
			433 (0.187)	(64%)
			432 (0.726)	HOMO-2 $\rightarrow$ LUMO+2
			419 (0.076)	(/1%)
				(72%)
		H <sub>2</sub> Corr-	610 (0.4421)	HOMO → LUMO (93%)
	427/444/535/588/635		538 (0.0141)	HOMO-1 → LUMO (76%)
DMSO			420 (1.1261)	HOMO $\rightarrow$ LUMO+1 (76%)
			389 (1.3104)	HOMO-1 → LUMO+1 (91%)



**Fig. SI36.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for Me-H in THF.



Fig. SI37. Orbital contours of the HOMO and LUMO for Me-H – tautomer 1 (T1), in THF.



Fig. SI38. Orbital contours of the HOMO and LUMO for Me-H – tautomer 2 (T2), in THF.



**Fig. SI39.** UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for Me-H in DMSO.



**Fig. SI40.** Orbital contours of the HOMO and LUMO for Me-H – deprotonated (H<sub>2</sub>Corr<sup>-</sup>), in DMSO.



Fig. SI41. UV-Vis Absorption experimental (Exp.) and theoretical (Calc.) spectra for Me-H in acetonitrile.





Fig. SI42. Orbital contours of the HOMO and LUMO for Me-H – "dimer" (aggregate), in acetonitrile.



**Fig. SI43.** Optimized structure for T1 and T2 of the Model corrole. Panel A front view, Panel B, perspective view.



**Fig. SI44.** Optimized structure for T1 and T2 of the Ph-H corrole. Panel A front view, Panel B, perspective view.



**Fig. SI45.** Optimized structure for the deprotonated Model corrole. Panel A front view, Panel B, perspective view.



**Fig. SI46.** Optimized structure of the deprotonated Ph-H corrole. Panel A front view, Panel B, perspective view.



**Fig. SI47.** Optimized structure of the homoconjugate complex for the Model corrole in acetonitrile. Panel A front view, Panel B, perspective view.



**Fig. SI48.** Optimized structure of the homoconjugate complex for Ph-H in acetonitrile. Panel A front view, Panel B, perspective view.

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