Electronic Supplementary Information

The Design of Dihalogenated TPE Monoboronate

Complexes as Mechanofluorochromic Crystals

Ma. Carmen García-González,^a* Armando Navarro-Huerta,^a Fanny Chantal Rodríguez-Muñoz,^a Estefania Vera-Alvizar,^a Marco A. Vera Ramirez,^b Joelis Rodríguez-Hernández,^c Mario Rodríguez^d and Braulio Rodríguez-Molina^a.*

^aInstituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior S.N.,

Ciudad Universitaria, Coyoacán, Ciudad de México, 04510, México

^bLaboratorio de RMN, Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, Iztapalapa, C.P. 09340 Ciudad de México, México

^cCentro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna Hermosillo No. 140, Saltillo, Coahuila 25294, Mexicoç

^dCentro de Investigaciones en Óptica, CIO, Apdo., Postal 1-948, 37000 León Gto, México

*M.C.G.G. e-mail: mcgg@unam.mx

*B. R. M. e-mail: brodriguez@iquimica.unam.mx

Table of Contents

EXPERIMENTAL SECTION	
GENERAL PROCEDURE FOR THE SYNTHESIS OF SCHIFF BASES Melting points and representative IR bands	
SOLUTION NMR SPECTRA	
X-RAY DIFFRACTION STUDIES	
CRYSTALLOGRAPHIC DATA	
SOLID-STATE PHOTOLUMINESCENCE SPECTRA AND TAUC PLOTS	
THEORETICAL COMPUTATIONS	
PXRD DIFFRACTOGRAMS	
LEBAIL FITTING METHOD OF THE SAMPLES EXPOSED TO DCM VAPORS	
REFERENCES	

Experimental Section

General procedure for the synthesis of Schiff Bases

Equimolar quantities of amine **1** and the appropriate amine were added into a round-bottom flask using methanol, the reaction was stirred under reflux for 1 hour, the solid obtained was filtered and washed with hexane and recrystallized with DCM/ EtOH.

2,4-dichloro-6-(((4-(1,2,2-triphenylvinyl)phenyl)imino)methyl)phenol (2a)



The title compound was prepared according to general procedure from **1** (0.300 g, 0.863 mmol) and 3,5-dichlorosalicylaldehyde (0.165 g, 0.863 mmol) to give **2a** (0.332 g, 74% yield) as an yellow solid, m.p. 195-197 °C. **IR** (v_{max} , cm⁻¹): 3060, 3054, 1619, 1444, 872, 848, 744, 698. ¹H NMR (300 MHz, CDCl₃) δ : 14.35 (s, 1H), 8.50 (s, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.15-7.04 (m, 19H). ¹³C NMR (75 MHz, CDCl₃) δ : 159.5, 156.3, 144.6, 144.0, 143.6 (2C), 143.5, 142.0, 140.0, 132.8 (2C), 131.5 (2C), 129.7, 128.0 (2C), 127.8, 126.9, 126.8 (2C), 123.4, 123.0, 120.7, 120.3. **HRMS** (DART+) calculated for C₃₃H₂₄Cl₂NO [M+H]⁺ 520.1234; found 520.1210.

2,4-dibromo-6-(((4-(1,2,2-triphenylvinyl)phenyl)imino)methyl)phenol (2b)



The title compound was prepared according to general procedure from **1** (0.300 g, 0.863 mmol) and 3,5-dibromosalicylaldehyde (0.242 g, 0.863 mmol) to give **2b** (0.469 g, 89% ield) as a red solid, **m.p.** 155-156 °C. **IR** (v_{max} , cm⁻¹): 3465, 3054, 1617, 1475, 850, 830, 754, 699. **¹H NMR** (300 MHz, CDCl₃) δ : 14.51 (s, 1H), 8.47 (s, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.43 (d, $J = 2.4 \text{ Hz}, 1\text{H}, 7.11-7.04 \text{ (m, 19H)}. \ ^{13}\text{C NMR} (75 \text{ MHz}, \text{CDCl}_3) \ \delta: 159.2, 157.7, 144.5, 144.1, 143.6 (2C), 143.5, 142.0, 140.0, 138.1, 133.4, 132.8, 131.5, 131.4, 128.0 (2C), 127.8, 126.9, 126.8 (2C), 120.8, 120.7, 112.4, 110.3.$ **HRMS**(DART+) calculated for C₃₃H₂₄Br₂NO [M+H]⁺ 608.0219; found 608.0237.

2,4-diiodo-6-(((4-(1,2,2-triphenylvinyl)phenyl)imino)methyl)phenol (2c)



The title compound was prepared according to general procedure from **1** (0.030 g, 0.863 mmol) and 3,5-diiodosalicylaldehyde (0.323 g, 0.863 mmol) to give **2c** (0.546 g, 90% yield) as a red solid, **m.p.** 145-146 °C. **IR** (v_{max} , cm⁻¹): 3443, 3053, 1749, 1613, 1586, 1438, 864, 818, 751, 700. ¹H NMR (300 MHz, CDCl₃) δ : 14.76 (s, 1H), 8.38 (s, 1H), 8.06 (d, J = 2.1 Hz, 1H), 7.60 (d, J = 2.1 Hz, 1H), 7.12-7.02 (m, 19H). ¹³C NMR (75 MHz, CDCl₃) δ : 160.7, 158.8, 149.1, 144.3, 144.0, 143.6, 143.5, 142.0, 140.5, 140.0, 132.8, 131.5 (2C), 128.0(2C), 127.8, 126.9, 126.8 (2C), 120.7 (2C), 87.7, 79.9. **HRMS** (DART+) calculated for C₃₃H₂₄I₂NO [M+H]⁺ 702.9947; found 703.9923.

Melting points and representative IR bands

Compound	Melting point (°C)	O-H _{stretching} (cm ⁻¹)	C=N _{stretching} (cm ⁻¹)
2a	195-197	3460	1619
2b	155-156	3465	1617
2c	145-146	3443	1613
3 a	235-237	-	1631
3b	220-221	-	1628
3 c	185-186	-	1624
4 a	236-238	-	1620
4b	223-225	-	1615
4 c	238-240	-	1622

Table S1. Melting point of compounds and IR stretching vibration of functional groups



Figure S2. ¹³C NMR of compound 2a in CDCl₃ at 75 MHz.



Figure S3. ¹H NMR of compound **2b** in CDCl₃ at 300 MHz.





Figure S6. ¹³C NMR of compound 2c in CDCl₃ at 75 MHz.



Figure S7. ¹H NMR of compound 3a in CDCl₃ at 400 MHz



Figure S8. ¹H NMR of compound 3b in CDCl₃ at 300 MHz



Figure S10. ¹H NMR of compound 3c in CDCl₃ at 300 MHz



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure S11. ¹³C NMR of compound 3c in CDCl₃ at 75 MHz.



Figure S12. ¹H NMR of compound 4a in CDCl₃ at 400 MHz





Figure S14. ¹H NMR of compound 4c in CDCl₃ at 400 MHz

X-Ray diffraction studies

Data collections were performed on a Bruker D8 diffractometer equipped with a PHOTON II CPAD detector with synchrotron radiation (Beamline 12.2.1 at Advanced Light Source, Lawrence Berkeley National Laboratory), and on a Bruker D8 Venture equipped with Smart APEX II CCD¹ with MoK α or CuK α radiation. The refinement of unit cell was made using SAINT V8.38A.² The structures were solved by direct methods and refined using SHELXL-2014.³ Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions using a riding model, with isotropic thermal parameters $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic hydrogens and $1.5U_{eq}(C)$ for hydroxyls. Images and crystal structures were generated with Mercury 2020.3.1.⁴

For Powder X-Ray Diffraction collections, the samples were grounded in an agate mortar and the loose powder was pressed into a diffractometer sample holder. The diffraction patterns were collected in Bragg-Brentano geometry at room temperature with CuK α radiation ($\lambda = 1.54183$ Å) in an Ultima IV diffractometer (from Rigaku) equipped with a D/teX detector. The patterns of samples were recorded from 4 to 60° (20) and 5°/min scan speed. The cell parameters were refined using the Le Bail pattern fitting method using the FULLPROF program.⁵ Peak profiles were calculated within ten times the full width at half maximum (FWHM) and pseudo-Voigt peak shape functions. The background was modeled by a third-order polynomial fitting. The structural data for each phase was obtained from their respective CIF. The obtained patterns for **4b** and **4b** after DCM vapors were indexed using the DICVOL and TREOR programs.^{6,7}

Crystallographic data

Table S2. Selected crystallographic information from the X-ray structures

Compound	2b	2c	3 a	3c	4c
Formula	C33H23Br2NO·C4H8O	C33H23I2NO·C3H6O	C37H31BCl2F2NO	C ₃₇ H ₃₁ BI ₂ F ₂ NO	C45H32BI2NO
Formula weight	681.45	761.40	568.22	751,12	867.32
Temperature (K)	296(2)	298(2)	150(2)	100(2)	200(2)
System	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space Group	P-1	P-1	P-1	P-1	P-1
a (Å)	9.4088(7)	9.330(3)	6.0896(4)	6.2357(3)	10.864(4)
b (Å)	12.5525(9)	12.726(3)	9.3799(6)	9.7731(4)	12.004(4)
c (Å)	15.2532(11)	15.427(3)	24.4891(15)	24.6541(10)	14.739(5)
α (°)	71.5265(15)	72.271(10)	84.352(2)	79.7070(10)	99.378(10)
β (°)	77.3805(15)	76.816(12)	86.909(2)	88.857(2)	91.705(10)
γ (°)	71.2592(15)	70.156(10)	87.232(2)	85.753(2)	91.595(10)
ρ (g/cm ³)	1.411	1.556	1.359	1.692	1.520
V (Å ³)	1604.3(2)	1625.2(7)	1388.70(15)	1474.20(11)	1894.5(12)
Z	2	2	2	2	2
Abs coefficient (mm ⁻¹)	2.559	15.437	0.275	2.294	1.695
F(000)	692	748	584	728	856
Crystal size (mm)	0.529 x 0.341 x 0.198	0.355 x 0.240 x 0.106	0.350 x 0.094 x 0.069	0.140 x 0.020 x 0.015	0.385 x 0.096 x 0.067
Radiation (Å)	ΜοΚα (0.71073)	ΜοΚα (0.71073)	ΜοΚα (0.71073)	Synchrotron (0.7288)	ΜοΚα (0.71073)
Collected reflections	24786	20040	37443	44417	47545
Independent reflections	5863	5926	7777	11143	10586
Data/rest/param	5863/250/428	5926/0/374	7777/0/361	11143/0/361	10586/0/451
GooF	1.044	1.044	1.018	1.151	1.024
Final R indexes	$R_1 = 0.0489$	$R_1 = 0.0495$	R ₁ =0.0613	R ₁ =0.0305	R ₁ =0.0557
$[I_0 > 2\sigma(I_0)]$	wR ₂ =0.1378	wR ₂ =0.1183	wR ₂ =0.1016	wR ₂ =0.0604	wR ₂ =0.1352
Final R indexes	R ₁ =0.0576	R ₁ =0.0664	R ₁ =0.1301	R ₁ =0.0343	R ₁ =0.1126
[all data]	wR ₂ =0.1451	wR ₂ =0.1304	wR ₂ =0.1212	wR ₂ =0.0634	wR ₂ =0.1629
Diff. peak/hole (eA-3)	1.169/-0.885	1.248/-0.921	0.329/-0.287	0.728/-0.678	1.625/-0.770
CCDC number	2075068	2075069	2075070	2075071	2075072



Figure S15. a) Overlap of crystal structures of compounds **2b** (blue) and **2c** (red), showing isostructurality. The angle formed by the planes of the halogenated ring and the TPE-bonded fragment in b) **2b** and c) **2c**. Thermal ellipsoids set at 50% level probability.



Figure S16. Overlapp of crystal structures of compounds **3a** and **3c**, showing isostructurality. Thermal ellipsoids set at 50% level probability.



Solid-state photoluminescence spectra and Tauc plots

Figure S17. Solid-state photoluminescence spectra and Tauc plots of compounds 3b and 3c.



Figure S18. Solid-state photoluminescence spectra and Tauc plots of compounds 4a and 4b.

Theoretical computations



Figure S19. Optimized molecular structures of compounds a) 2a, b) 2b and 2c.



Figure S20. Optimized molecular structures of compounds a) 3a, b) 3b and 3c.



Figure S21. Optimized molecular structures of compounds a) 4a, b) 4b and 4c.



Figure S22. Frontier Molecular Orbitals (FMO) of compounds **2a**, **3a** and **4a**, calculated at the level of theory B3LYP/6-31G(d)



Figure S23. Frontier Molecular Orbitals (FMO) of compounds **2b**, **3b** and **4b**, calculated at the level of theory B3LYP/6-31G(d).



Figure S24. Frontier Molecular Orbitals (FMO) of compounds **2c**, **3c** and **4c**, calculated at the level of theory B3LYP/LANL2DZ.



Figure S25. 350 - 550 nm window from the experimental absorption profiles for the crystalline solid of **3a** (panel a) and its ground counterpart (panel b), shown as a solid black line. The profile was fitted with a sum (red dashed line) of three gaussian functions centered at λ_1 - λ_3 values.



Figure S26. a) Agreement between experimental excitation wavelengths and those calculated using TDDFT for the crystalline and ground states of 3a; b) Changes in the intensity of each excitation wavelength because of grinding.



Figure S27. Frontier molecular orbitals, corresponding to λ_3 in **3a** calculated at the B3LYP(D3)/def2TZVP level of theory. Surfaces are displayed at a 0.04 isocontour.



Figure S28. Experimental powder diffractograms of compound **3a**: a) Before grinding, b) Ground powder, and c) After exposure to DCM vapors.



Figure S29. Experimental powder diffractograms of compound **3c**: a) Before grinding, b) Ground powder, and c) After exposure to DCM vapors.



Figure S30. Experimental powder diffractograms of compound **4a**: a) Before grinding, b) Ground powder, and c) After exposure to DCM vapors.



Figure S31. Experimental powder diffractograms of compound **4b**: a) Before grinding, b) Ground powder, and c) After exposure to DCM vapors.



LeBail fitting method of the samples exposed to DCM vapors

Figure S32. LeBail fitting of the experimental powder X-Ray diffraction of **3a**: a) As synthesized, and b) After exposure to DCM vapors. Cell parameters taken from CIF.



Figure S33. LeBail fitting of the experimental Powder X-Ray Diffraction of **4b**: a) As synthesized, and b) After exposure to DCM vapors. Cell parameters taken from CIF.



Figure S34. LeBail fitting of the experimental Powder X-Ray Diffraction of **4c**: a) As synthesized, and b) After exposure to DCM vapors. Cell parameters taken from CIF.



Figure S35. LeBail fitting of the experimental Powder X-Ray Diffraction of 3c.

Compound	Reference (CIF)	Initial parameters	%Powdered sample	Final parameters (After DCM vapors)
3 a	a = 6.0896(4) Å	a = 6.093(1) Å		a = 6.120(1) Å
	b = 9.3799(6) Å	b = 9.368(2) Å		b = 9.396(2) Å
	c = 24.4891(15) Å	c = 24.622(6) Å		c = 24.865(6) Å
	$\alpha = 84.352(2)^{\circ}$	$\alpha = 85.14(1)^{\circ}$	100%	$\alpha = 85.08(1)^{\circ}$
	$\beta = 86.909(2)^{\circ}$	$\beta = 86.65(1)^{\circ}$		$\beta = 86.46(1)^{\circ}$
	$\gamma = 87.232(2)^{\circ}$	$\gamma = 87.75(1)^{\circ}$		$\gamma = 87.67(1)^{\circ}$
	$V = 1388.70(15) Å^3$	$V = 1397.4(5) Å^3$		$V = 1420.8(6) Å^3$
	a = 6.2357(3) Å	a = 6.164(1)Å		
	b = 9.7731(4) Å	b = 9.753(2)Å		
Зс	c = 24.6541(10) Å	c = 24.512(4)Å		Different crystalline phase than initial
	$\alpha = 79.7070(10)^{\circ}$	$\alpha = 79.99(1)^{\circ}$	100%	
	$\beta = 88.857(2)^{\circ}$	$\beta = 89.57(1)^{\circ}$		
	$\gamma = 85.753(2)^{\circ}$	$\gamma = 86.18(1)^{\circ}$		
	$V = 1474.20(11) Å^3$	$V = 1448.0(4) Å^3$		
				Same phase as initial,
4 a			85%	changes in intensity of
		0		reflections
4b*		a = 12.483(1) A		a = 12.485(3) A
		b = 21.454(3) A	1000	b = 21.465(5) A
		c = 9.34/(1) A	100%	c = 9.318(2) A
		$\beta = 97.16(1)^{\circ}$		$\beta = 97.06(1)^{\circ}$
	10.064(4) 8	$V = 2483.7(5) A^{3}$		$V = 2478(1) A^{3}$
4c	a = 10.864(4) A	a = 10.838(3) A		a = 10.851(1) A
	b = 12.004(4) A	b = 12.025(3) A		b = 12.000(1) A
	c = 14.739(5) A	c = 14./12(3) A	1000/	c = 14.722(1) A
	$\alpha = 99.3/8(10)^{\circ}$	$\alpha = 99.34(1)^{\circ}$	100%	$\alpha = 99.40(1)^{\circ}$
	$\beta = 91.705(10)^{\circ}$	$\beta = 91.64(1)^{\circ}$		$\beta = 91.61(1)^{\circ}$
	$\gamma = 91.595(10)^{\circ}$	$\gamma = 91.40(1)^{\circ}$		$\gamma = 91.46(1)^{\circ}$
	$V = 1894.5(12) A^{3}$	$V = 1890.3(7) A^{3}$		$V = 1889.5(3) A^{3}$

Table S3. Summary of LeBail fitting parameters for compounds herein reported.

*Cell parameters obtained from DICVOL and TREOR softwares.

References

- S1. APEX2 Version 2008.3-0/2.2-0, Bruker AXS, Inc., Madison, WI, 2007.
- S2. Bruker. (2006b). SAINT, Version 8.38 (Bruker AXS Inc.).
- S3. G. M. Sheldrick, Acta Cryst. A., 2008, 64, 112–122.
- S4. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.*, 2020, **53**, 226–235.
- S5. J. Rodríguez-Carvajal, "*The FullProf Program*", Institute Leon Brillouin, Saclay, France, 2000.
- S6. A. Boultif and D. Louer. J. Appl. Crystallogr., 1991, 24, 987.
- S7. P.E. Werner, L. Ericksson and M. Westdahl, J. Appl. Cryst., 1985, 18, 367–370.