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Supporting Information for

Solid-emissive fluorophores constructed by a non-planar heteropolycyclic structure with bulky substituents: synthesis and X-ray crystal structures

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X-ray crystal structure analyses. X-ray crystal structure analyses of **2a**–**2c** and **3a**–**3c**: The data sets were collected at 23 ± 1 ˚C on a Rigaku AFC7S four-circle diffractometer by 2θ-ω scan technique, and using graphite-monochromated Mo-Kα (λ = 0.71069 Å) radiation at 50 kV and 30 mA. In all case, the data were corrected for Lorentz and polarization effects. A correction for secondary extinction was supplied. The reflection intensities were monitored by three standard reflections for every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. All calculations were performed using the teXsan[1] crystallographic software package of Molecular Structure Corporation.

Crystal of **2a** was recrystallized from a mixture solvent of dichloromethane and *n*-hexane as yellow prism, air stable. The one selected had approximate dimensions 0.40×0.40×0.50 mm. The transmission factors ranged from 0.86 to 0.99. The crystal structure was solved by direct methods using SIR 92.[2] The structures were expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.
Crystal data for **2a**: $C_{34}H_{39}NO_2$, M = 493.69, momoclinic, a = 14.321(2), b = 11.583(3), c = 17.877(2) Å, β = 104.490(8)˚, U = 2871.3(9) Å^3, T = 296.2K, space group $P2_1/n$ (no.14), Z = 4, μ(Mo-K_a) = 0.70 cm^{-1}, 5552 reflections measured, 5047 unique (R_{int} = 0.042) which were used in all calculations. The final R indices were R1 = 0.074, wR (F^2) = 0.183 (all data).

Crystal of guest-free **2b** was recrystallized from a mixture solvent of dichloromethane and *n*-hexane as yellow prism, air stable. The one selected had approximate dimensions 0.70×0.10×0.40 mm. The transmission factors ranged from 0.96 to 1.00. The crystal structure was solved by direct methods using SIR 92.[2] The structures were expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms

were refined isotropically, the rest were fixed geometrically and not refined.
Crystal data for **2b**: $C_{36}H_{35}NO_2$, M = 513.68, momoclinic, a = 9.081(2), b = 20.626(4), c = 15.600(3) Å, β = 98.69(2)°, U = 2888(1) Å^3, T = 296.2K, space group $P2_1/c$ (no.14), Z = 4, μ(Mo-K_a) = 0.72 cm^{-1}, 5427 reflections measured, 5087 unique (R_{int} = 0.059) which were used in all calculations. The final R indices were R1 = 0.055, wR (F^2) = 0.174 (all data).

Crystal of **2c** was recrystallized from a mixture solvent of dichloromethane and *n*-hexane as yellow prism, air stable. The one selected had approximate dimensions 0.60×0.50×0.10 mm. The transmission factors ranged from 0.87 to 1.00. The crystal structure was solved by direct methods using SIR 92.[2] The structures were expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.
Crystal data for **2c**: $C_{34}H_{33}NO_2S$, M = 519.70, triclinic, a = 10.088(8), b = 16.317(6), c = 9.031(6) Å, α = 91.18(4)°, β = 97.28(6)°, γ = 72.73(4)°, U = 1407(1) Å^3, T = 296.2K, space group P1- (no.2), Z = 2, μ(Mo-K_a) = 1.46 cm^{-1}, 6872 reflections measured, 6463 unique (R_{int} = 0.084) which were used in all calculations. The final R indices were R1 = 0.094, wR (F^2) = 0.194 (all data).

Crystal of **3a** was recrystallized from a mixture solvent of dichloromethane and *n*-hexane as orange prism, air stable. The one selected had approximate dimensions 0.20×0.20×0.40 mm. The transmission factors ranged from 0.97 to 1.00. The crystal structure was solved by direct methods using SIR 92.[2] The structures were expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.
Crystal data for **3a**: $C_{34}H_{39}NO_2$, M = 493.69, momoclinic, a = 9.471(5), b = 30.489(6), c = 10.734(5) Å, β = 114.03(3)°, U = 2830(2) Å^3, T = 296.2K, space group $P2_1/a$ (no.14), Z = 4, μ(Mo-K_a) = 0.71 cm^{-1}, 5417 reflections measured, 4981 unique (R_{int} = 0.050) which were used in all calculations. The final R indices were R1 = 0.053, wR (F^2) = 0.117 (all data).

Crystal of **3b** was recrystallized from a mixture solvent of dichloromethane and *n*-hexane as orange prism, air stable. The one selected had approximate dimensions 0.20×0.10×0.45 mm. The transmission factors ranged from 0.95 to 1.00. The crystal structure was solved by direct methods using SAPI91.[4] The structures were expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.
Crystal data for **3b**: $C_{36}H_{35}NO_2$, M = 513.68, orthorhombic, a = 20.947(7), b = 31.759(7), c =

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8.758(7) Å, U = 5826(4) $Å^3$, T = 296.2K, space group Pbca (no.61), Z = 8, μ(Mo-K_a) = 0.71 cm^{-1}, 5385 reflections measured, 4786 unique (R_{int} = 0.000) which were used in all calculations. The final R indices were R1 = 0.055, wR (F^2) = 0.108 (all data).

Crystal of **3c** was recrystallized from a mixture solvent of dichloromethane and *n*-hexane as orange prism, air stable. The one selected had approximate dimensions 0.50×0.40×0.40 mm. The transmission factors ranged from 0.87 to 1.00. The crystal structure was solved by direct methods using SIR 92.[2] The structures were expanded using Fourier techniques.[3] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined.
Crystal data for **3c**: $C_{34}H_{33}NO_2S$, M = 519.70, triclinic, a = 11.009(2), b = 13.949(5), c = 9.752(2) Å, α = 97.99(2)°, β = 101.46(2)°,γ = 72.82(2)°, U = 1397.1(6) $Å^3$, T = 296.2K, space group P1- (no.2), Z = 2, μ(Mo-K_a) = 1.47 cm^{-1}, 6801 reflections measured, 6426 unique (R_{int} = 0.040) which were used in all calculations. The final R indices were R1 = 0.0793, wR (F^2) = 0.184 (all data).

1. teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation 1985 and 1992.

2. A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Cryst*., 1994, **27**, 435.

3. DIRDIF94. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, The DIRIF94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

4. Fan Hai-Fu (1991). Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.

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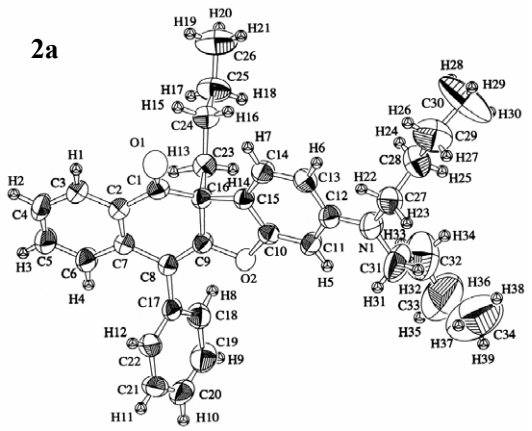
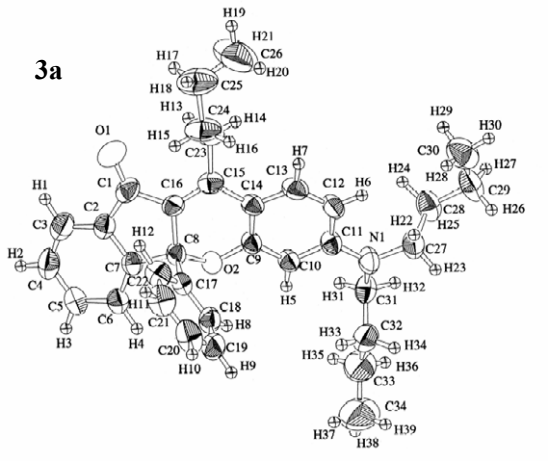
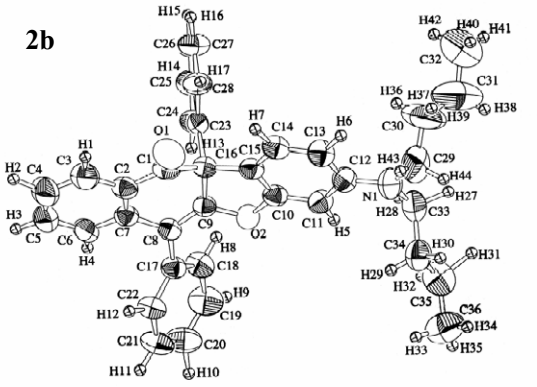
2a



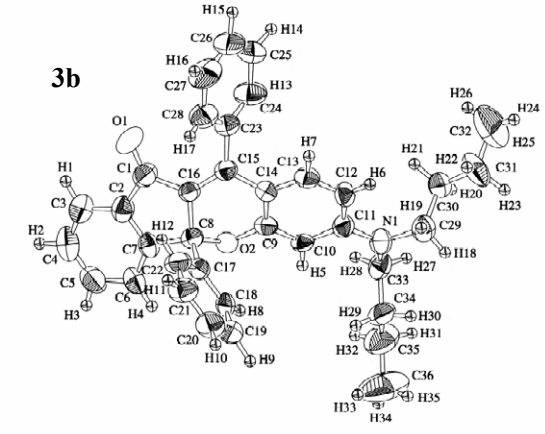
3a



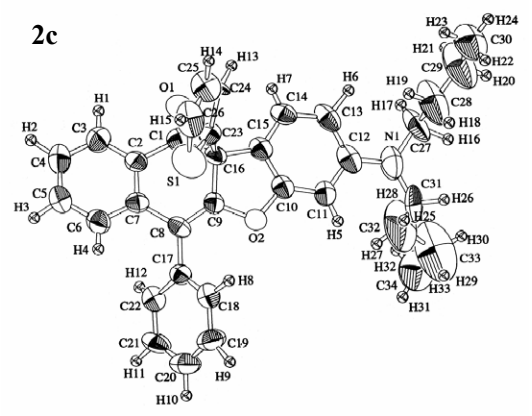
2b



3b



2c



3c

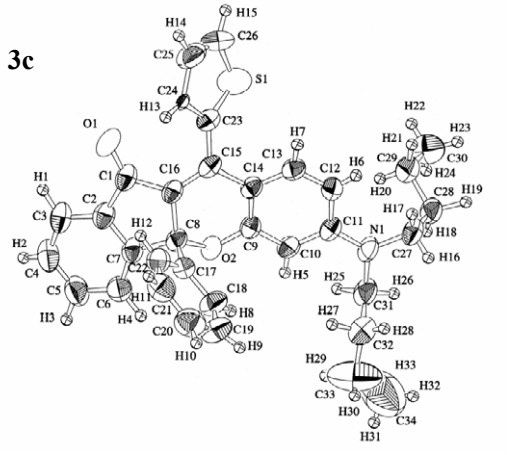


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Table S1 Crystal data and structure refinement parameter for the compounds **2a**-**2c** and **3a**-**3c**.

Compound	**2a**	**3a**
Molecular formula	$C_{34}H_{39}NO_2$	$C_{34}H_{39}NO_2$
Formula weight	493.69	493.69
Number of reflection used for unit cell determination (2θ range/°)	25 (23.7-27.4)	25 (22.0-24.7)
Crystal System	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$
a/Å	14.321(2)	9.471(5)
b/Å	11.583(3)	30.489(6)
c/Å	17.877(2)	10.734(5)
α/°		
β/°	104.490(8)	114.03(3)
γ/°		
V/Å^3	2871.3(9)	2830(2)
Z	4	4
D_c/g cm^{-3}	1.142	1.158
F(000)	1064.00	1064.00
M(Mokα)/cm^{-1}	0.70	0.71
Crystal dimensions/nm	0.40×0.40×0.50	0.20×0.20×0.40
Scan mode	ω-2θ	ω-2θ
Scan rate in ω/°min^{-1}	8.0(up to 5 scans)	8.0(up to 5 scans)
Scan width/°	1.57 + 0.30 tanθ	0.79 + 0.30 tanθ
2θ max/°	50.0	50.0
Range of induces *h*; *k*; *l*	0, 17; 0, 13; -21, 20	-11, 0; 0, 36; -11, 12
Reflections collected (unique)	5047	4981
Reflection observed with $I_0>2\sigma I_0$	2461	2071
Number of parameters	407	459
R	0.074	0.053
R_w	0.183	0.117
w	$(\sigma^2F^2)^{-1}$	$(\sigma^2F^2)^{-1}$
S	1.75	1.10
Max. Shift/Error in final cycle	0.001	0.005
Max. peak in final diff. map/e Å^{-3}	0.37	0.21
Min. peak in final diff. map/e Å^{-3}	-0.32	-0.22

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Compound	**2b**	**3b**
Molecular formula	$C_{36}H_{35}NO_2$	$C_{36}H_{35}NO_2$
Formula weight	513.68	513.68
Number of reflection used for unit cell determination (2θ range/°)	25 (22.2-25.5)	12 (22.1-23.9)
Crystal System	monoclinic	orthorhombic
Space group	$P2_1/c$	Pbca
a/Å	9.081(2)	20.947(7)
b/Å	20.626(4)	31.759(7)
c/Å	15.600(3)	8.758(7)
α/°		
β/°	98.69(2)	
γ/°		
V/Å^3	2888(1)	5826(4)
Z	4	8
D_c/g cm^{-3}	1.181	1.171
F(000)	1096.00	2192.00
M(Mokα)/cm^{-1}	0.72	0.71
Crystal dimensions/nm	0.70×0.10×0.40	0.20×0.10×0.45
Scan mode	ω-2θ	ω-2θ
Scan rate in ω/°min^{-1}	4.0(up to 5 scans)	8.0(up to 5 scans)
Scan width/°	1.78 + 0.30 tanθ	0.79 + 0.30 tanθ
2θ max/°	50.0	50.0
Range of induces *h*; *k*; *l*	-10, 0; 0, 24; ±18	0, 22; 0, 37; -10, 0
Reflections collected (unique)	5087	4786
Reflection observed with $I_0>2\sigma I_0$	1900	1284
Number of parameters	457	465
R	0.055	0.055
R_w	0.174	0.108
w	$(\sigma^2F^2)^{-1}$	$(\sigma^2F^2)^{-1}$
S	1.21	1.00
Max. Shift/Error in final cycle	0.05	0.003
Max. peak in final diff. map/e Å^{-3}	0.40	0.83
Min. peak in final diff. map/e Å^{-3}	-0.21	-0.87

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Compound	**2c**	**3c**
Molecular formula	$C_{34}H_{33}NO_2S$	$C_{34}H_{33}NO_2S$
Formula weight	519.70	519.70
Number of reflection used for unit cell determination (2θ range/°)	7 (22.5-24.5)	20 (25.1-34.0)
Crystal System	triclinic	triclinic
Space group	P1-	P1-
a/Å	10.088(8)	11.009(2)
b/Å	16.317(6)	13.949(5)
c/Å	9.031(6)	9.752(2)
α/°	91.18(4)	97.99(2)
β/°	97.28(6)	101.46(2)
γ/°	72.73(4)	72.82(2)
V/Å^3	1407(1)	1397.1(6)
Z	2	2
D_c/g cm^{-3}	1.226	1.235
F(000)	552.00	552.00
M(Mokα)/cm^{-1}	1.46	1.47
Crystal dimensions/nm	0.60×0.50×0.10	0.50×0.40×0.40
Scan mode	ω-2θ	ω-2θ
Scan rate in ω/°min^{-1}	8.0(up to 5 scans)	8.0(up to 5 scans)
Scan width/°	1.68 + 0.30 tanθ	1.47 + 0.30 tanθ
2θ max/°	55.0	55.0
Range of induces *h*; *k*; *l*	±13; ±21; -11, 0	-14, 14; -18, 17; 0, 12
Reflections collected (unique)	6463	6426
Reflection observed with $I_0>2\sigma I_0$	1656	2675
Number of parameters	392	432
R	0.094	0.079
R_w	0.194	0.184
w	$(\sigma^2F^2)^{-1}$	$(\sigma^2F^2)^{-1}$
S	1.36	1.63
Max. Shift/Error in final cycle	0.03	0.002
Max. peak in final diff. map/e Å^{-3}	1.14	0.54
Min. peak in final diff. map/e Å^{-3}	-1.02	-0.43