Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Supramolecular organization and optical properties of BODIPY derivatives in Langmuir–Schaefer films

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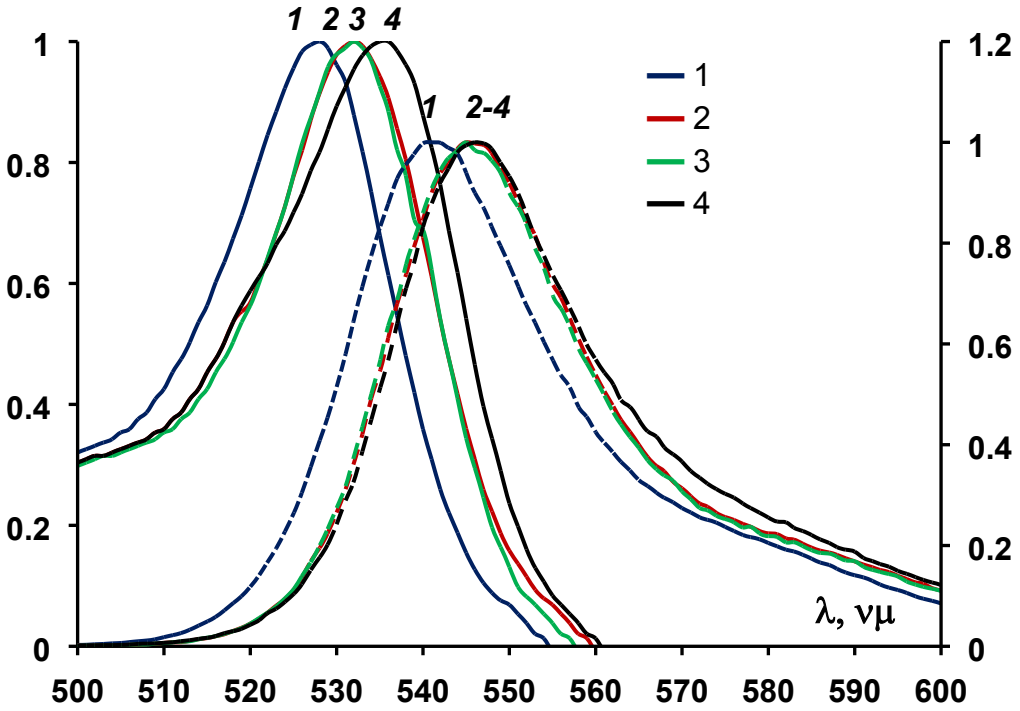


Figure S1. UV–Vis EAS (solid lines) and fluorescence spectra (dashed lines) of investigated dyes in benzene; numeration indicates the spectra of the corresponding compounds (data reprinted from the following article: Y. S. Marfin, O. S. Vodyanova, D. A. Merkushev, S. D. Usoltsev, V. O. Kurzin and E. V. Rumyantsev, J. Fluoresc., 2016, 26, 1975–1985.)

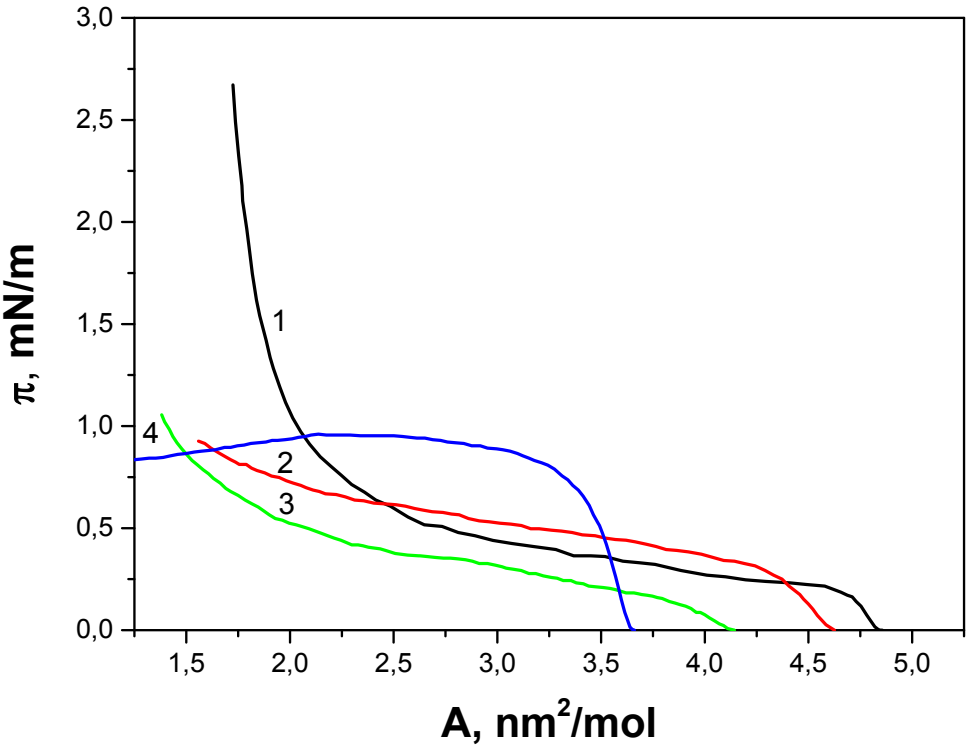


Figure S2. Surface pressure–area (π−A) isotherms of investigated dyes during LS-films deposition; numeration indicates the spectra of the corresponding compounds.

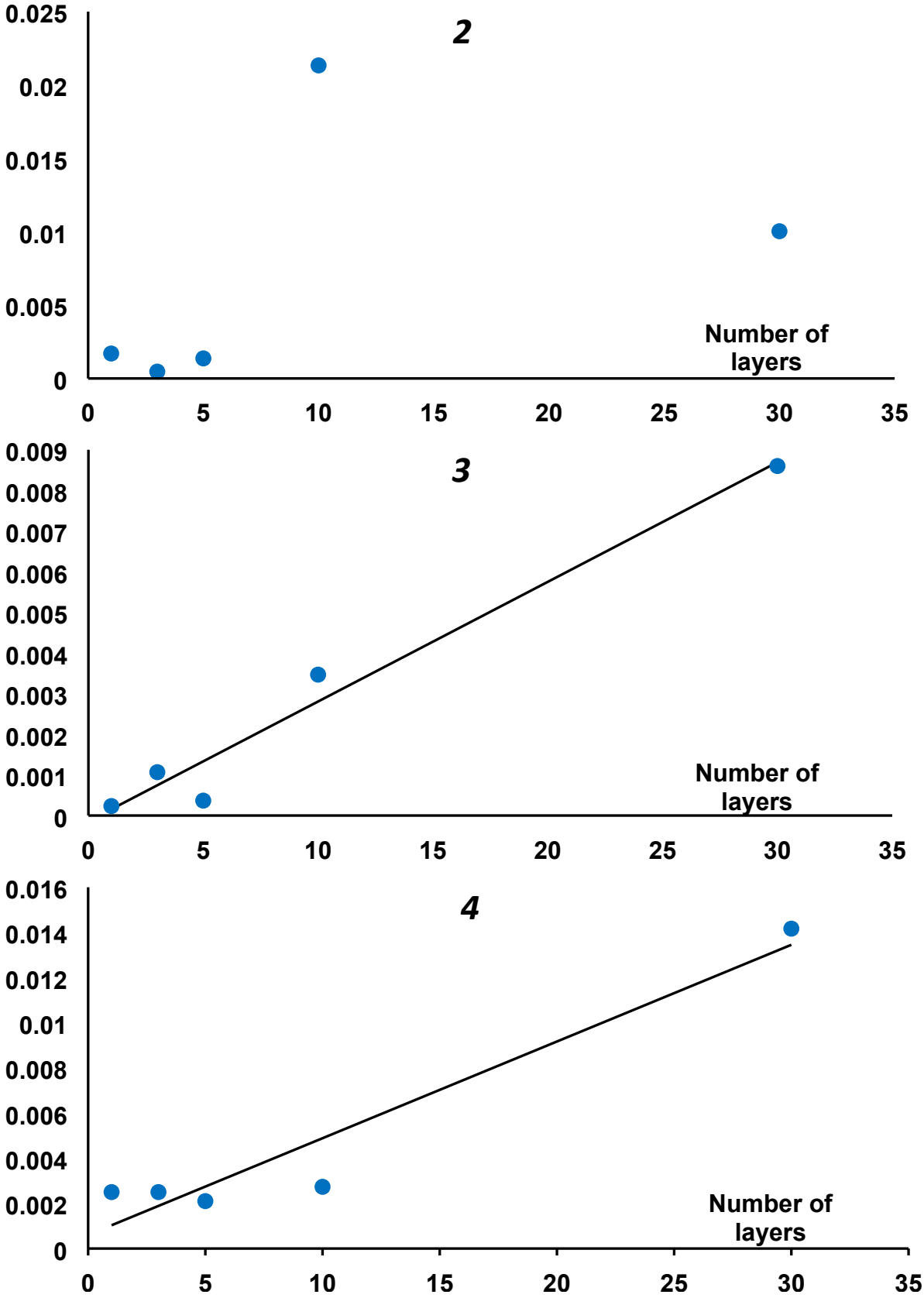


Figure S3. Correlation of films' optical absorbance with number of BODIPY layers: *2* – films of the compound ***2***, *3* – films of the compound ***3*** (R^2 = 0.9699), *4* – films of the compound ***4*** (R^2 = 0.9264).

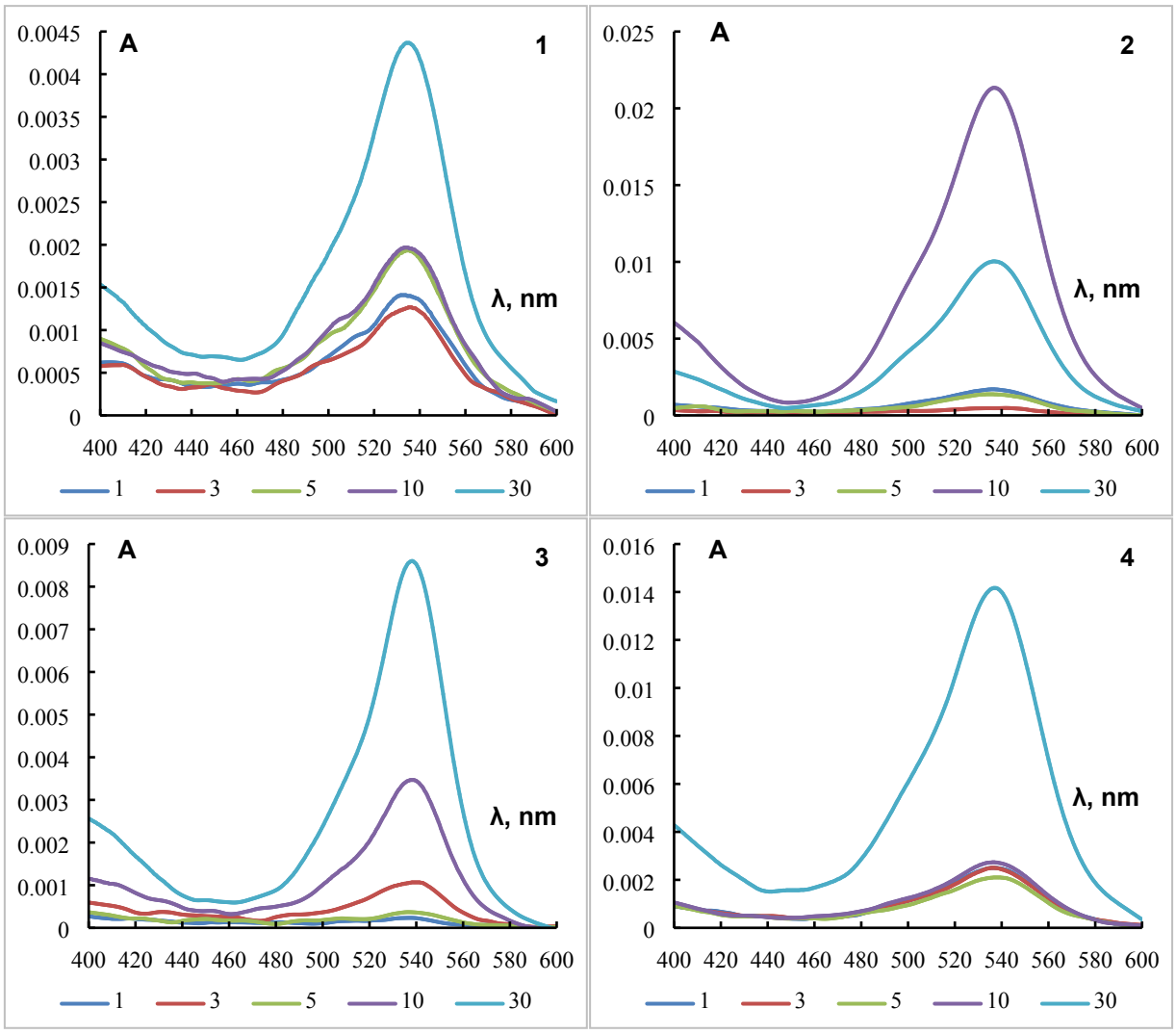


Figure S4. Absorption spectra of BODIPYs **1-4** (number in the top right corner) films with different number of dye layers.

Table S1. Fluorescence intensity changes after 10 min exposition in solvent vapor for compound ***2***.

Solvent	Relative fluorescence $I_{max(solvent)}/I_{max(dry\ film)}$
C_2H_5OH (Ethanol)	0.997
C_6H_{12} (Cyclohexane)	0.954
C_6H_6 (Benzene)	1.006
$CHCl_3$ (Chloroform)	1.017

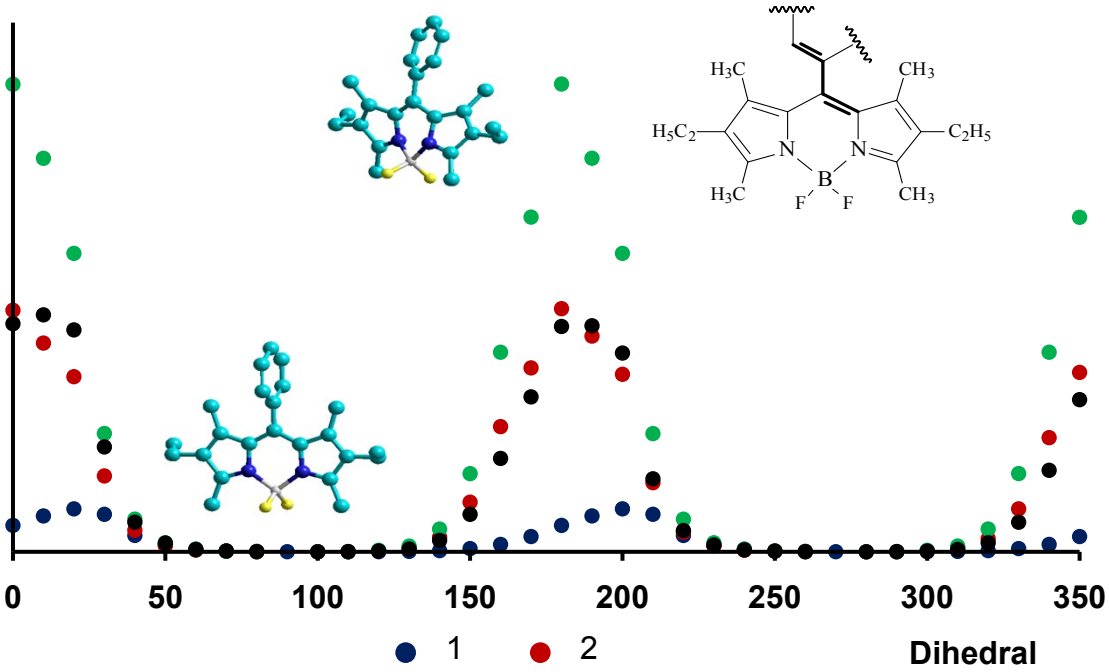
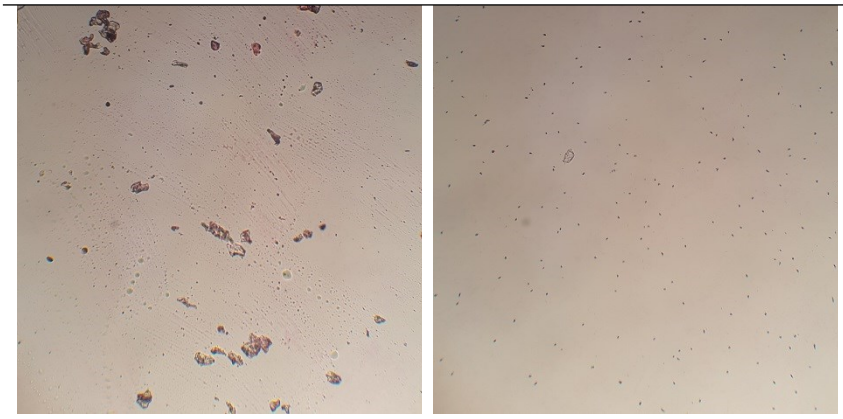


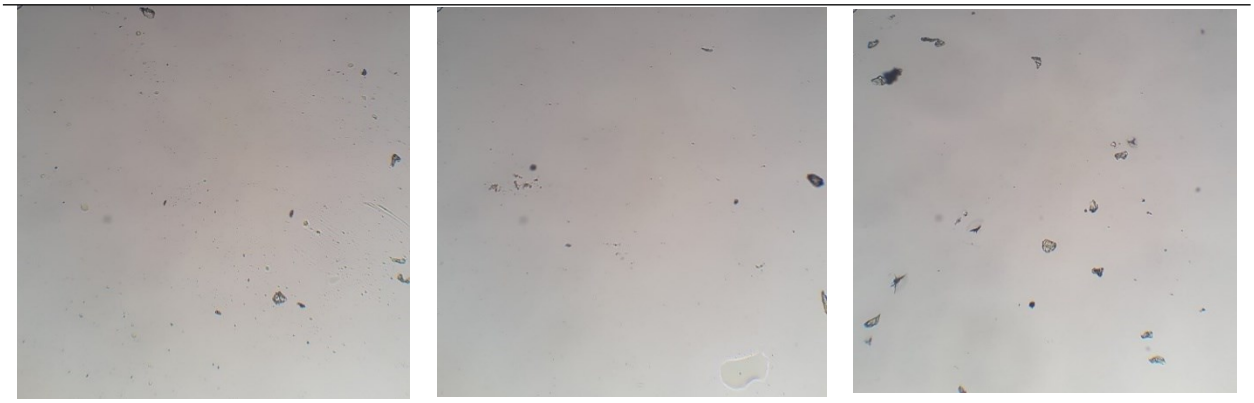
Figure S5. The potential energy surfaces of BODIPY dyes as a function of 8-substituent rotation and optimized geometries for ***1*** in lowest and highest energy points.

1 layer 3 layers 5 layers

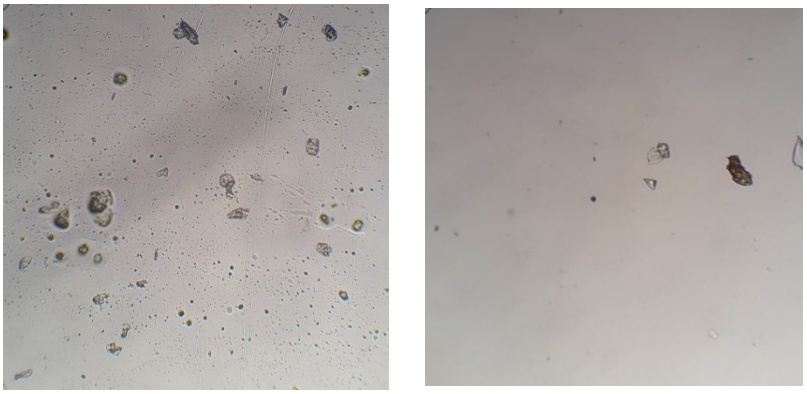


10 layers 30 layers

Figure S6. Microphotographs of compound ***2*** thin films on glass surface (1.0 mm).

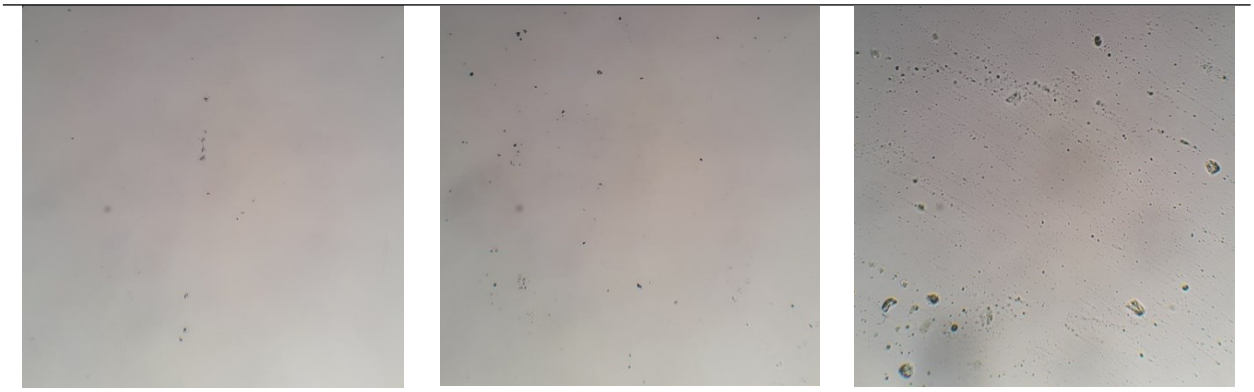


1 layer 3 layers 5 layers

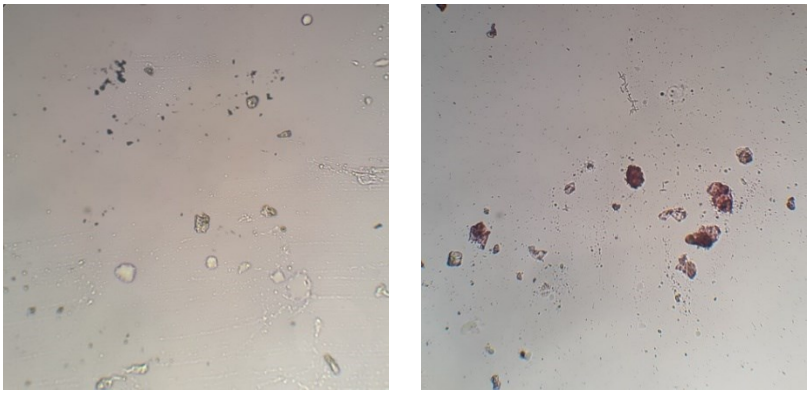


10 layers 30 layers

Figure S7. Microphotographs of compound ***3*** thin films on glass surface (1.0 mm).

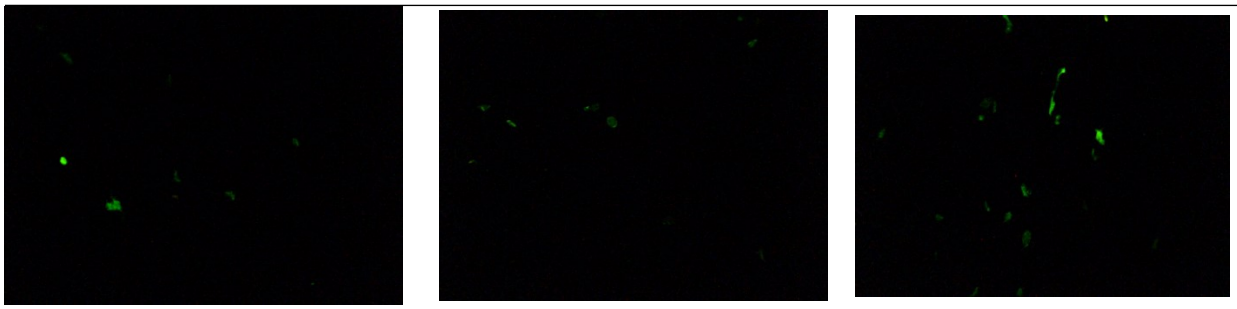


1 layer 3 layers 5 layers



10 layers 30 layers

Figure S8. Microphotographs of compound ***4*** thin films on glass surface (1.0 mm).



1 layer 3 layers 5 layers

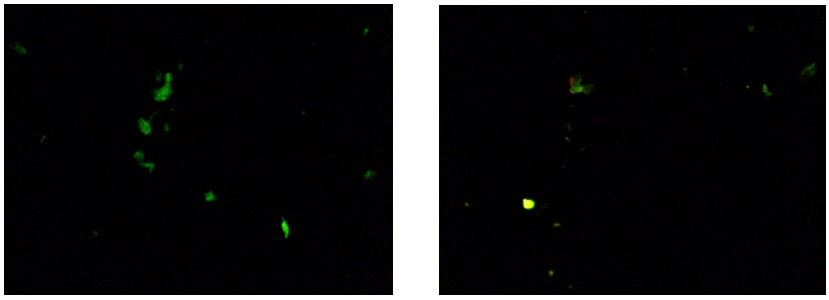


Figure S9. Fluorescent microphotographs of compound ***3*** thin films on glass surface (1.0 mm), λ_{ex} = 410–490 nm.

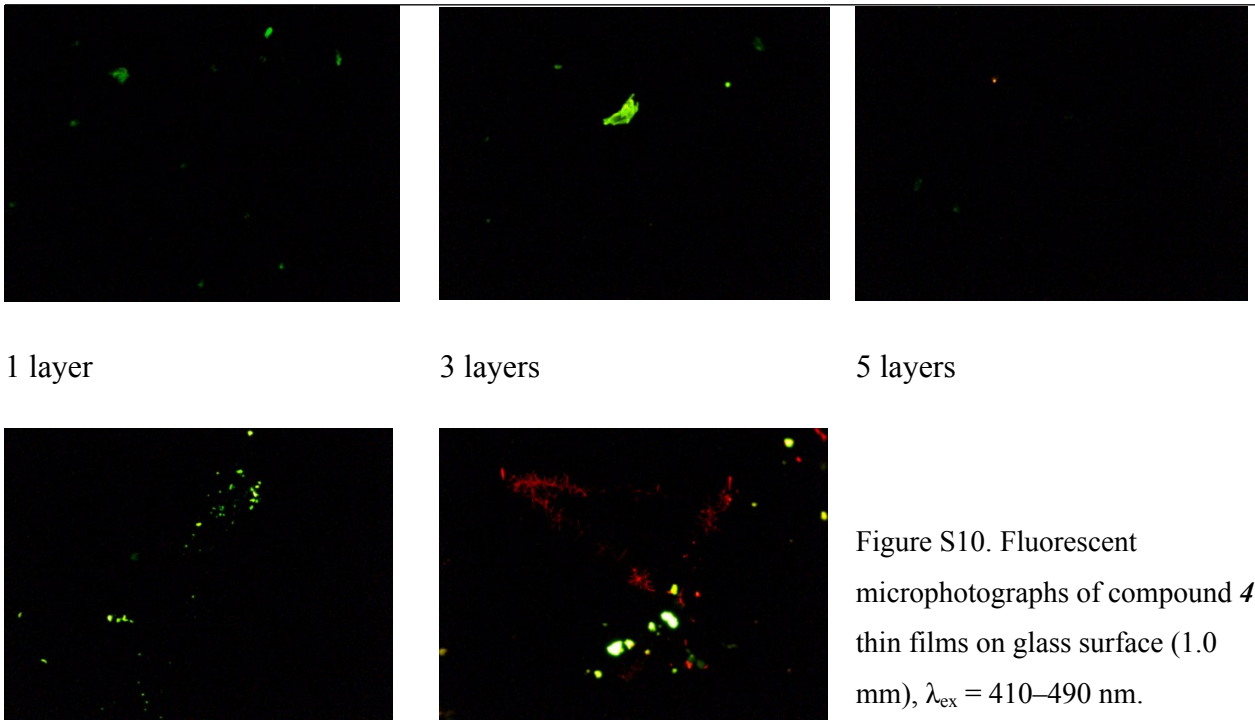
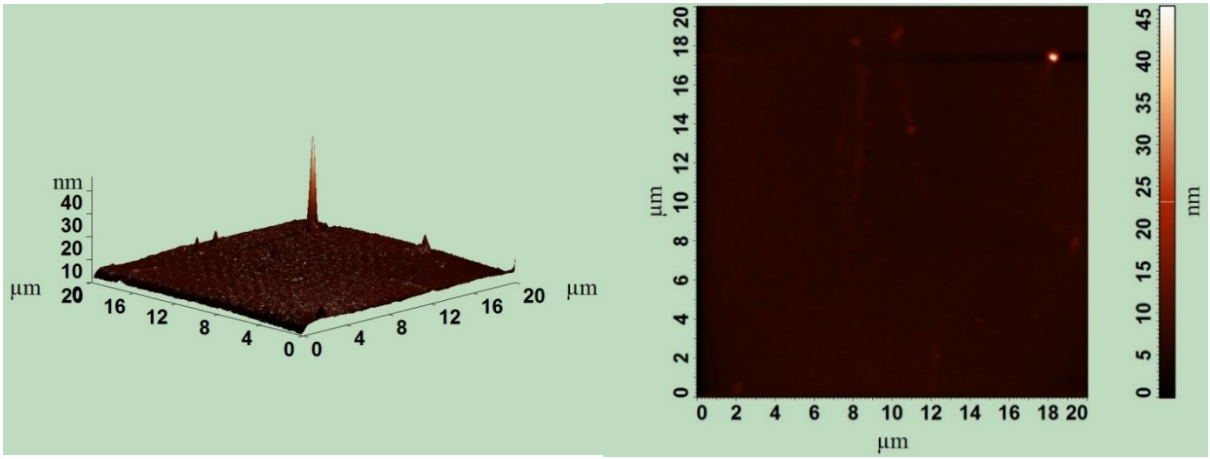
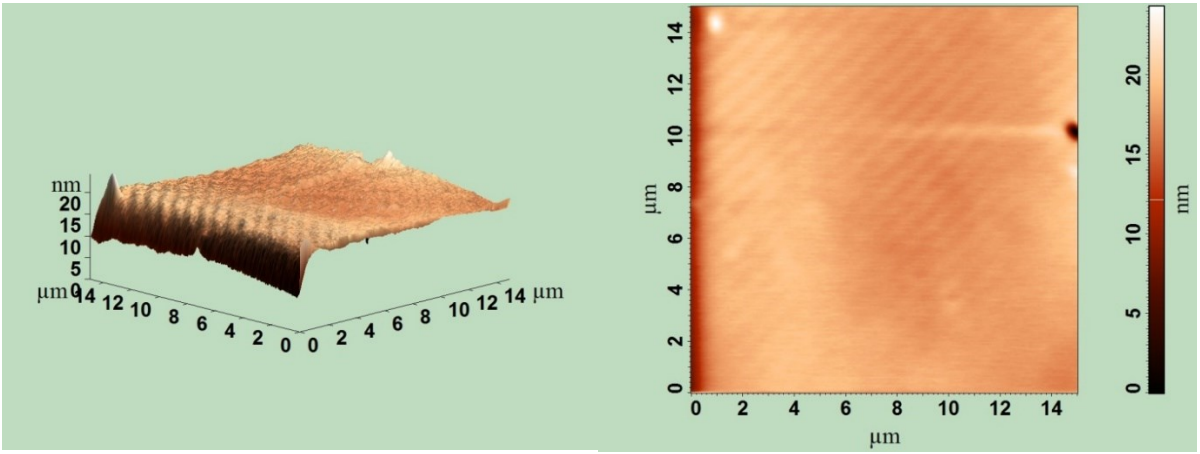


Figure S10. Fluorescent microphotographs of compound ***4*** thin films on glass surface (1.0 mm), λ_{ex} = 410–490 nm.

Table S2. AFM images and experimental details for LB-films.

Compound *3*	
1 layer	
Amount of sampling	65536
Max	46.374 nm
Min	0 nm
Peak-to-peak, Sy	46.374 nm
Ten point height, Sz	22.1604 nm
Average	5.57531 nm
Average Roughness, Sa	0.474706 nm
Second moment	5.6537
Root Mean Square, Sq	0.938246 nm
Surface skewness, Ssk	12.4259
Coefficient of kurtosis, Ska	439.095
Entropy	4.72368
Redundance	0.14174
	
10 layers	
Amount of sampling	65536
Max	24.249 nm
Min	0 nm
Peak-to-peak, Sy	24.249 nm
Ten point height, Sz	12.3458 nm
Average	17.9652 nm

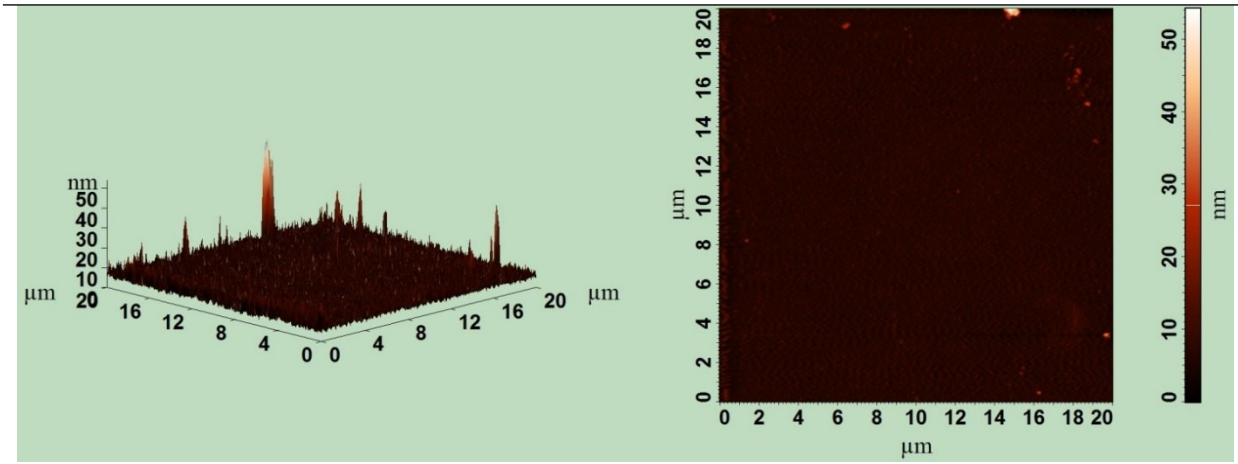
Average Roughness, Sa	0.93784 nm
Second moment	18.0229
Root Mean Square, Sq	1.44016 nm
Surface skewness, Ssk	-2.77385
Coefficient of kurtosis, Ska	15.0205
Entropy	5.57183
Redundance	-0.22752



Compound 4

1 layer

Amount of sampling	65536
Max	54.162 nm
Min	0 nm
Peak-to-peak, Sy	54.162 nm
Ten point height, Sz	26.1606 nm
Average	6.72587 nm
Average Roughness, Sa	1.32176 nm
Second moment	7.02489
Root Mean Square, Sq	2.02776 nm
Surface skewness, Ssk	5.2314
Coefficient of kurtosis, Ska	76.4763
Entropy	6.17343
Redundance	-0.0769513



10 layers

Amount of sampling	65536
Max	18.408 nm
Min	0 nm
Peak-to-peak, Sy	18.408 nm
Ten point height, Sz	9.1863 nm
Average	14.2484 nm
Average Roughness, Sa	0.886185 nm
Second moment	14.3273
Root Mean Square, Sq	1.50176 nm
Surface skewness, Ssk	-3.65142
Coefficient of kurtosis, Ska	24.0364
Entropy	5.5749
Redundance	-0.35258

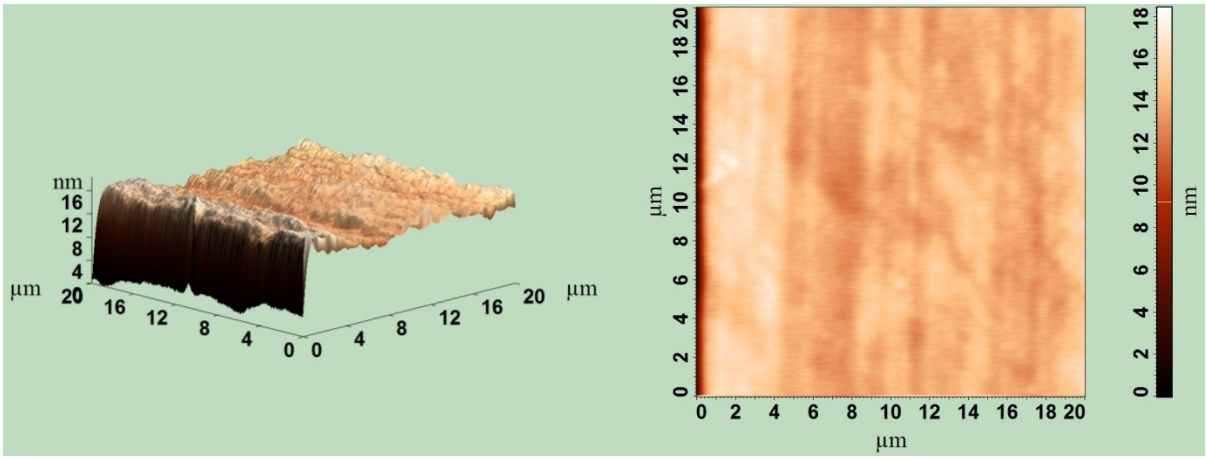


Table S3. Crystal data, details of data collection and parameters of structure refinement for BODIPY ***4*** single crystal.

Compound	$C_{33}H_{31}BF_2N_2$
T, K	293
M	504.4
Crystal system, space group, Z	Monoclinic, $P2_1/n$, 4
a, b, c, Å	7.8921(3), 25.8630(10), 15.1136(8)
β, deg	92.072(4)
V, Å^3	3082.8(3)
D_x, g/cm^3	1.087
Diffractometer	Xcalibur, Eos S2 CCD
Radiation; λ, Å	MoK_α; 0.71069
Scan mode	ω
μ, mm^{-1}	0.038
Crystal size max × mid × min, mm	0.638 × 0.261 × 0.129
Absorption correction; T_{min}, T_{max}	Analytical; 0.985, 0.997
θ_{max}, deg	25.27
Limiting indices	$-9 \le h \le 8$, $-31 \le k \le 31$, $-18 \le l \le 18$
Number of reflections: measured/unique (N_1), R_{int}/with $I > 3\sigma(I)$ (N_2)	68042/5558, 0.147/2278
Refinement method	Least squares on F
Weighting scheme	$1/\sigma^2(F) + 0.0036F^2$
Number of parameters	343
R/R_w for N_1	0.1741/0.1397
R/R_w for N_2	0.0626/0.1020
S_{all}	1.19
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	–0.28/0.42
Programs	CrysAlis, JANA2006

Table S4. Atomic coordinates and isotropic equivalent atomic displacement parameters (U_{iso}) in the structure of BODIPY ***4*** single crystal

Atom	x/a	y/b	z/c	U_{iso}, Å^2
F1	0.3070(3)	0.6513(1)	0.8400(2)	0.086(1)
F2	0.1687(3)	0.6592(1)	0.7079(2)	0.089(1)

N1	0.3538(3)	0.7277(1)	0.7550(2)	0.050(1)
N2	0.0809(3)	0.7132(1)	0.8273(2)	0.050(1)
B1	0.2295(6)	0.6858(2)	0.7821(3)	0.056(2)
C1	0.3975(5)	0.8741(2)	1.0435(3)	0.055(1)
C2	0.3694(4)	0.9274(1)	1.0601(2)	0.050(1)
C3	0.3353(4)	0.8513(1)	0.9692(2)	0.048(1)
C4	0.4299(5)	0.9514(2)	1.1382(3)	0.067(2)
C5	0.0885(5)	0.8868(2)	0.7626(3)	0.066(2)
C6	–0.1618(5)	0.7281(2)	0.8960(2)	0.055(1)
C7	0.0663(5)	0.9389(2)	0.7745(3)	0.073(2)
C8	–0.3236(5)	0.7171(2)	0.9411(3)	0.078(2)
C9	0.4022(6)	1.0036(2)	1.1521(3)	0.077(2)
C10	–0.0547(5)	0.6903(2)	0.8613(2)	0.059(2)
C11	0.5804(4)	0.7678(2)	0.6999(2)	0.058(2)
C12	0.5004(4)	0.7204(2)	0.7131(2)	0.055(1)
C13	0.1738(4)	0.8566(1)	0.8251(2)	0.048(1)
C14	–0.0870(4)	0.7750(2)	0.8841(2)	0.053(1)
C15	0.2406(4)	0.8795(1)	0.9027(1)	0.045(1)
C16	0.2790(4)	0.9573(1)	0.9958(2)	0.048(1)
C17	0.5134(6)	0.8628(2)	0.7324(3)	0.076(2)
C18	0.4784(5)	0.8060(2)	0.7350(2)	0.052(1)
C19	0.3168(56)	1.0330(2)	1.0873(3)	0.075(2)
C20	0.7425(5)	0.7757(2)	0.6523(3)	0.073(2)
C21	0.7117(5)	0.7886(2)	0.5566(3)	0.097(2)
C22	–0.1573(5)	0.8259(2)	0.9146(3)	0.075(2)
C23	–0.2967(6)	0.7095(3)	1.0411(4)	0.143(3)
C24	0.2160(4)	0.9332(1)	0.9153(2)	0.048(1)
C25	–0.0770(5)	0.6327(2)	0.8623(4)	0.089(2)
C26	0.1668(5)	1.0392(2)	0.9438(4)	0.074(2)
C27	0.1062(5)	1.0177(2)	0.8687(3)	0.074(2)
C28	0.5596(8)	0.6681(2)	0.6878(3)	0.086(2)
C29	0.2543(5)	1.0101(2)	1.0092(3)	0.057(1)
C30	0.1272(5)	0.9635(2)	0.8513(3)	0.060(2)
C31	0.3353(4)	0.7811(1)	0.7695(2)	0.048(1)
C32	0.0661(4)	0.7665(2)	0.8398(2)	0.049(1)
C33	0.1934(4)	0.7995(1)	0.8108(2)	0.047(1)
H1C1	0.4628	0.8540	1.0853	0.066
H1C3	0.3548	0.8150	0.9606	0.058
H1C4	0.4910	0.9315	1.1824	0.080
H1C5	0.0435	0.8708	0.7094	0.080
H1C7	0.0079	0.9587	0.7292	0.087
H1C8	–0.3757	0.6867	0.9157	0.094
H2C8	–0.4021	0.7449	0.9300	0.094
H1C9	0.4418	1.0195	1.2063	0.093
H1C17	0.4929	0.8777	0.7892	0.091
H2C17	0.6295	0.8685	0.7181	0.091
H3C17	0.4402	0.8788	0.6882	0.091
H1C19	0.3009	1.0694	1.0965	0.090
H1C20	0.8071	0.8029	0.6807	0.088
H2C20	0.8107	0.7450	0.6574	0.088
H1C21	0.8176	0.7888	0.5273	0.116

H2C21	0.6376	0.7633	0.5296	0.116
H3C21	0.6601	0.8222	0.5515	0.116
H1C22	–0.1441	0.8515	0.8693	0.091
H2C22	–0.2754	0.8220	0.9261	0.091
H3C22	–0.0971	0.8368	0.9677	0.091
H1C23	–0.3941	0.6928	1.0643	0.172
H2C23	–0.1981	0.6885	1.0526	0.172
H3C23	–0.2809	0.7426	1.0691	0.172
H1C25	–0.1774	0.6241	0.8932	0.107
H2C25	–0.0877	0.6201	0.8026	0.107
H3C25	0.0197	0.6170	0.8917	0.107
H1C26	0.1501	1.0755	0.9532	0.089
H1C27	0.0474	1.0389	0.8255	0.089
H1C28	0.6799	0.6688	0.6804	0.103
H2C28	0.5336	0.6438	0.7334	0.103
H3C28	0.5035	0.6578	0.6332	0.103

Note. All sites are fully occupied.

Table S5. Main interatomic distances in the structure of BODIPY ***4*** single crystal1.

Bond	Distance, Å	Bond	Distance, Å
B1–F1	1.378(5)	C10–C25	1.501(6)
–F2	1.385(5)	C11–C12	1.395(6)
–N1	1.528(6)	–C18	1.391(6)
–N2	1.551(5)	–C20	1.504(5)
N1–C12	1.352(5)	C12–C28	1.488(6)
–C31	1.405(5)	C13–C15	1.401(5)
N2–C10	1.343(5)	–C33	1.499(5)
–C32	1.396(5)	C14–C22	1.508(7)
C1–C2	1.421(5)	–C32	1.420(5)
–C3	1.339(5)	C15–C24	1.417(5)
C2–C4	1.401(6)	C16–C24	1.439(5)
–C16	1.414(5)	–C29	1.396(5)
C3–C15	1.430(5)	C17–C18	1.497(6)
C4–C9	1.385(7)	C18–C31	1.417(5)
C5–C7	1.373(6)	C19–C29	1.395(6)
–C13	1.382(5)	C20–C21	1.496(6)
C6–C8	1.497(5)	C24–C30	1.411(5)
–C10	1.406(6)	C26–C27	1.336(7)
–C14	1.362(6)	–C29	1.404(6)
C7–C30	1.373(6)	C27–C30	1.436(6)
C8–C23	1.531(7)	C31–C33	1.386(5)
C9–C19	1.394(7)	C32–C33	1.401(5)