

## ESI for

Marzena Banasiewicz,<sup>a</sup> Irena Deperasińska,<sup>a</sup> Artur Makarewicz,<sup>a</sup> Dikhi Firmansyah,<sup>b</sup> Daniel T. Gryko<sup>b,c,\*</sup> and Bolesław Kozankiewicz<sup>a,\*</sup>, *Why vertically  $\pi$ -expanded imidazo[1,2-*a*]pyridines are weak fluorescence emitters: experimental and computational study.*

Table S1. Calculated electronic transition energies ( $\Delta E$ ) and their oscillator strengths (*f*). Graphical presentations are given on the right side. The lowest energy singlet  $\pi\pi^*$  states are located at 38498  $\text{cm}^{-1}$  and at 38518  $\text{cm}^{-1}$  in compounds **2** and **3**, respectively. All other states are of  $\pi\pi^*$  type.

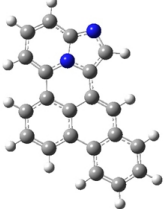
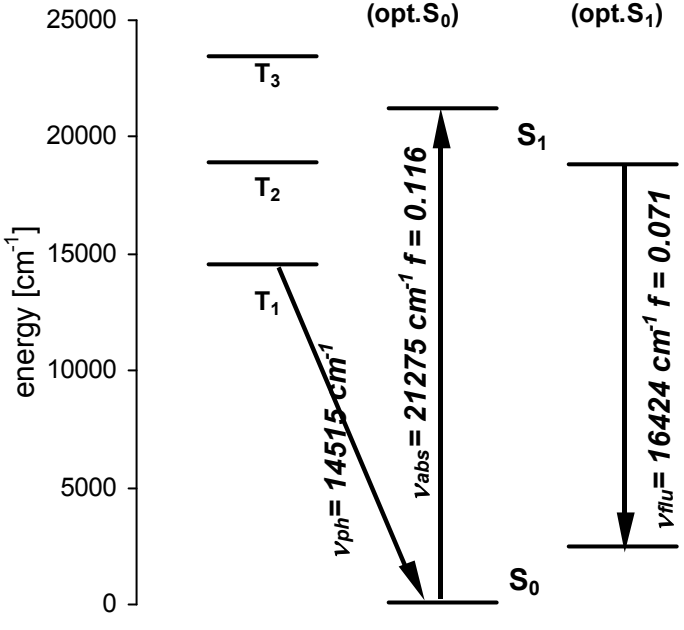
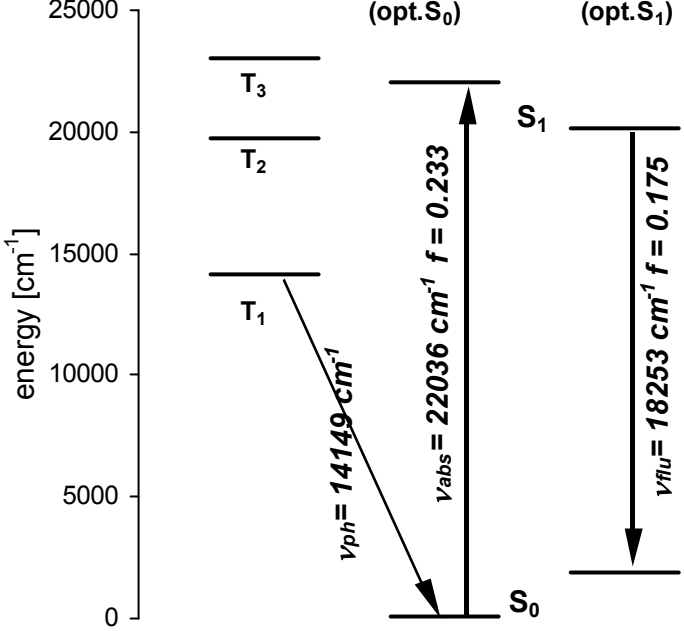
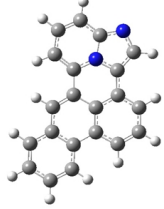
	$\Delta E$ [ $\text{cm}^{-1}$ ]	$\lambda$ [nm]	<i>f</i>	
		$S_0 \rightarrow S_i$		
	21275	470.0	0.1155	
	26383	379.0	0.0520	
	27125	368.7	0.2836	
	32125	311.3	0.0806	
	34655	288.6	0.1065	
	35377	282.7	0.0394	
	35910	278.5	0.0123	
	36868	271.2	0.0006	
38233	261.6	0.0523		
38498	259.8	0.0004		
	$S_1 \rightarrow S_0$			
16424	608.9	0.0706		
	$S_0 \rightarrow T_i$			
14615	684.2			
18932	528.2			
23455	426.3			
	$\Delta E$ [ $\text{cm}^{-1}$ ]	$\lambda$ [nm]	<i>f</i>	
		$S_0 \rightarrow S_i$		
	22036	453.1	0.0233	
	26281	380.5	0.0579	
	26638	375.4	0.0759	
	31536	317.1	0.1029	
	34462	290.2	0.0822	
	35710	280.0	0.0080	
	35856	278.9	0.0059	
	36688	272.6	0.0278	
38518	259.6	0.0003		
38544	259.4	0.1606		
	$S_1 \rightarrow S_0$			
18253	547.9	0.1747		
	$S_0 \rightarrow T_i$			
14149	706.8			
19736	506.7			
22994	434.9			

Table S2. Comparison of shapes of HOMO and LUMO orbitals of both isomers and the directions of their dipole moments

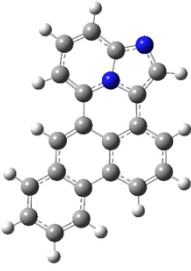
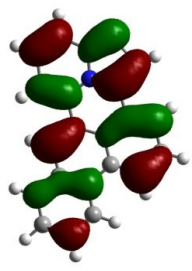
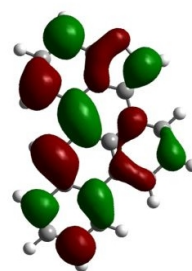
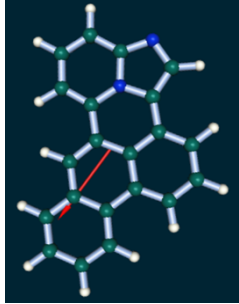
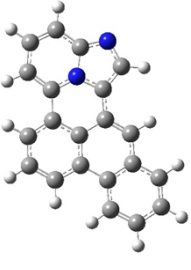
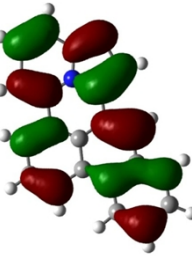
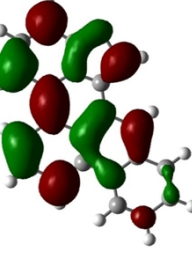
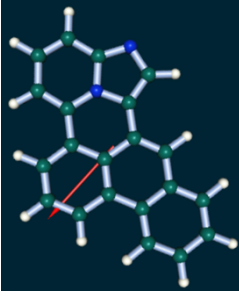
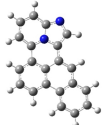
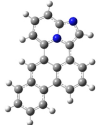
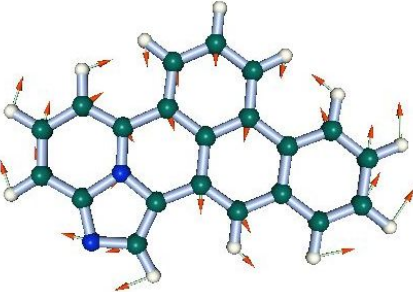
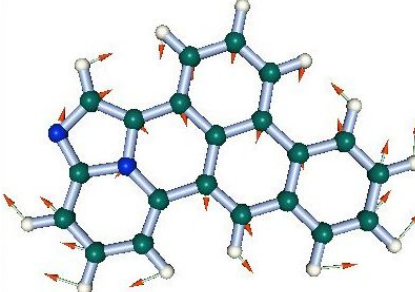
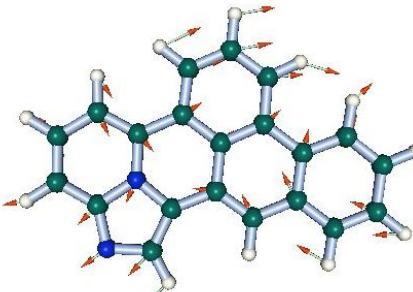
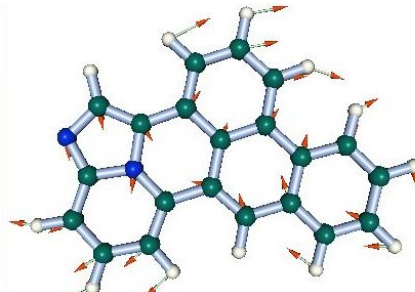
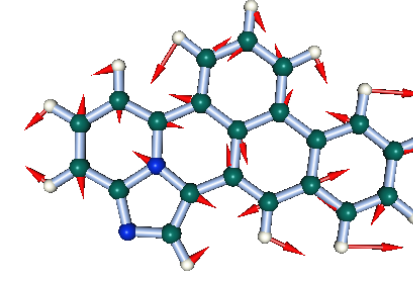
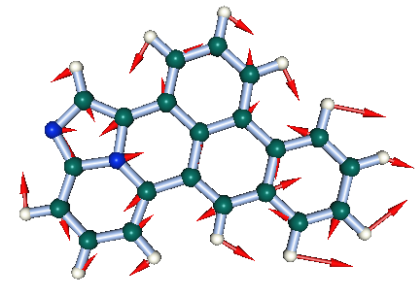
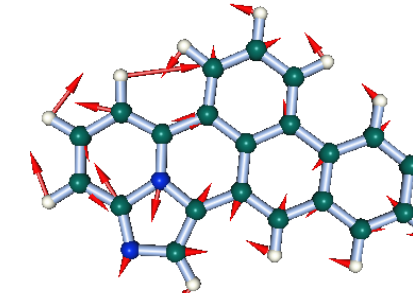
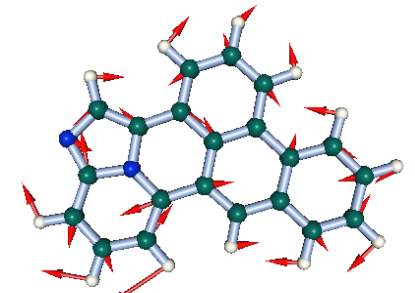
	HOMO	LUMO	dipole moment
			
			

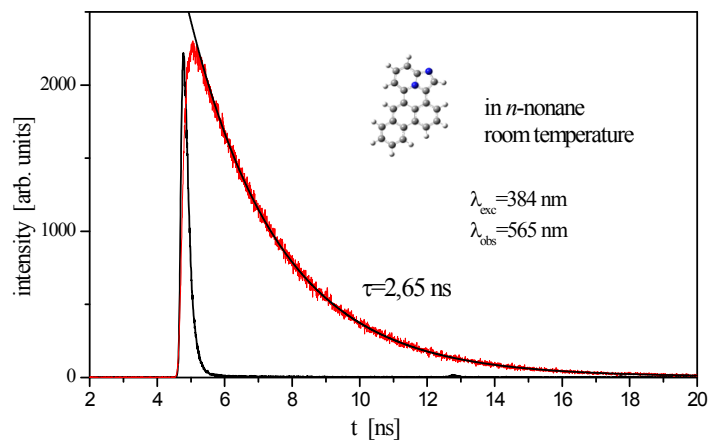
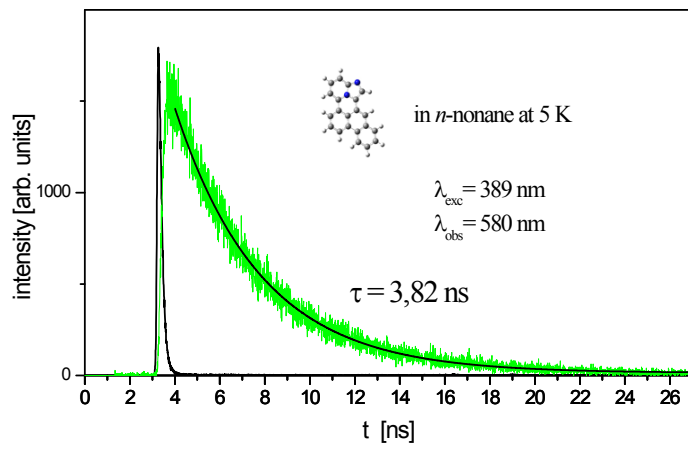
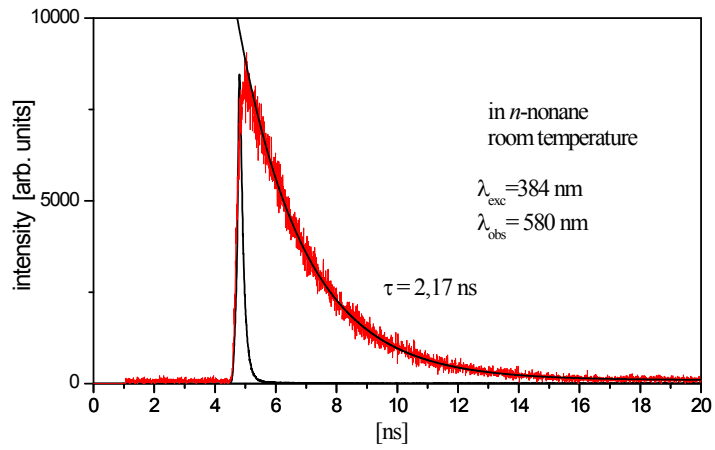
Table S3. Frequencies of vibrations calculated for optimized structures of compounds **2** and **3** in  $S_0$  and  $S_1$  electronic states. Vibrations active in the fluorescence spectra indicated in bold.

compound	<b>2</b>		<b>3</b>		compound	<b>2</b>		<b>3</b>	
electronic state	$S_0$	$S_1$	$S_0$	$S_1$	electronic state	$S_0$	$S_1$	$S_0$	$S_1$
mode number					mode number				
1	44.5	45.0	48.5	53.8	51	1059.5	1053.6	1056.1	1043.2
2	63.4	69.3	62.4	63.1	52	1070.1	1064.9	1065.1	1054.9
3	106.9	101.8	109.9	103.4	53	1082.7	1071.3	1082.6	1067.0
4	127.1	123.7	130.4	129.8	54	1100.4	1084.9	<b>1093.5</b>	1080.4
<b>5</b>	<b>178.4</b>	175.6	<b>179.1</b>	176.1	55	1130.9	1120.4	1120.1	1114.2
6	208.1	188.6	209.7	193.7	56	1149.1	1138.5	1159.7	1154.0
7	224.3	203.3	224.4	213.6	57	1174.2	1169.3	1181.3	1175.9
8	257.8	256.9	255.0	250.2	58	1192.1	1186.3	1188.3	1184.4
9	293.0	287.8	294.5	290.7	59	1195.8	1189.8	1193.7	1187.8
<b>10</b>	<b>299.8</b>	294.5	308.5	295.1	60	1213.6	1202.7	1209.1	1189.9
11	310.0	310.4	<b>318.8</b>	318.9	61	1229.6	1224.6	1224.0	1220.5
12	341.4	336.3	329.8	326.0	62	1236.1	1226.7	1245.6	1233.8
<b>13</b>	<b>362.6</b>	360.3	<b>357.2</b>	357.2	63	1245.8	1265.5	<b>1249.6</b>	1246.6
14	450.7	424.1	439.0	421.9	64	1290.2	1274.9	1280.1	1279.7
15	459.5	446.3	441.7	435.4	65	<b>1308.0</b>	1292.8	1310.1	1291.9
16	472.7	456.8	492.4	457.3	66	1320.0	1306.9	1331.4	1309.0
17	498.2	489.5	<b>506.2</b>	473.7	<b>67</b>	<b>1335.0</b>	1321.6	<b>1334.8</b>	1321.3
18	511.4	495.4	515.5	500.3	68	1362.9	1349.9	1363.4	1357.8
19	513.7	505.3	529.5	507.4	69	1364.9	1369.5	1364.3	1370.4
20	538.0	507.8	530.2	524.6	70	1368.8	1374.3	1372.1	1376.4
21	579.1	566.7	573.6	561.0	71	1386.9	1380.2	1388.9	1387.7
22	593.8	570.6	586.8	561.0	72	1393.1	1417.1	1396.2	1402.0
23	595.0	591.8	597.4	580.0	73	1423.1	1421.4	<b>1412.8</b>	1413.9
24	611.2	597.8	607.0	592.2	74	1431.8	1437.7	1434.2	1440.7
25	627.4	617.8	645.1	633.2	75	1469.7	1455.1	1471.3	1451.8
26	653.5	635.7	659.1	638.7	76	1480.4	1467.6	1482.5	1462.4
27	664.4	643.7	666.2	646.6	77	1500.0	1485.8	1494.9	1485.6
28	672.6	657.0	669.5	659.0	<b>78</b>	<b>1532.7</b>	1511.0	<b>1529.1</b>	1500.1
29	679.2	671.1	681.7	664.8	<b>79</b>	<b>1543.1</b>	1528.6	<b>1541.6</b>	1515.7
30	743.8	696.8	740.8	693.0	80	1560.5	1535.8	1569.9	1527.0
31	752.9	701.6	752.4	718.1	<b>81</b>	<b>1572.3</b>	1553.4	<b>1572.6</b>	1548.8
32	756.1	730.2	755.3	736.9	82	1586.9	1578.6	1585.3	1571.1
33	767.4	751.3	759.7	742.7	83	1623.4	1588.4	1625.1	1585.9
34	770.5	760.4	770.7	743.3	84	1644.8	1606.6	1647.8	1603.7
35	791.0	764.6	791.6	753.7	<b>85</b>	<b>1661.4</b>	1632.7	<b>1651.5</b>	1612.7
36	795.8	773.0	804.6	762.9	<b>86</b>	<b>1663.6</b>	1643.2	<b>1664.9</b>	1638.0
37	821.8	785.2	822.6	795.1	87	1675.9	1652.1	1677.0	1664.4
<b>38</b>	<b>856.0</b>	789.0	<b>835.4</b>	799.0	88	3177.7	3181.3	3177.3	3176.1
39	857.5	814.5	855.3	827.2	89	3187.0	3183.7	3187.3	3188.4
40	865.6	830.8	871.7	831.6	90	3189.4	3191.5	3188.9	3191.2
41	871.3	853.8	879.0	847.8	91	3191.9	3194.2	3197.0	3193.4
42	879.3	857.0	885.8	872.9	92	3201.9	3199.5	3203.0	3195.9
43	889.3	864.2	887.8	880.9	93	3204.2	3207.9	3203.8	3198.4
44	897.9	878.0	893.7	888.4	94	3211.2	3210.0	3205.5	3210.2
45	935.9	929.9	929.4	917.5	95	3214.9	3221.5	3213.8	3214.2

46	943.5	949.5	947.7	929.0	96	3228.9	3235.2	3229.4	3234.2
47	969.1	953.0	970.7	951.8	97	3235.5	3236.8	3235.7	3236.0
48	970.7	961.6	972.3	965.1	98	3239.8	3237.9	3239.5	3242.3
49	972.4	961.9	988.0	980.4	99	3248.5	3258.4	3247.2	3258.7
50	986.0	987.6	994.2	991.7					

Table S4. Graphical presentation of vibrations "170", "360", "1530" and "1540"  $\text{cm}^{-1}$  of both molecules

		
"170"		
"360"		
"1530"		
"1540"		



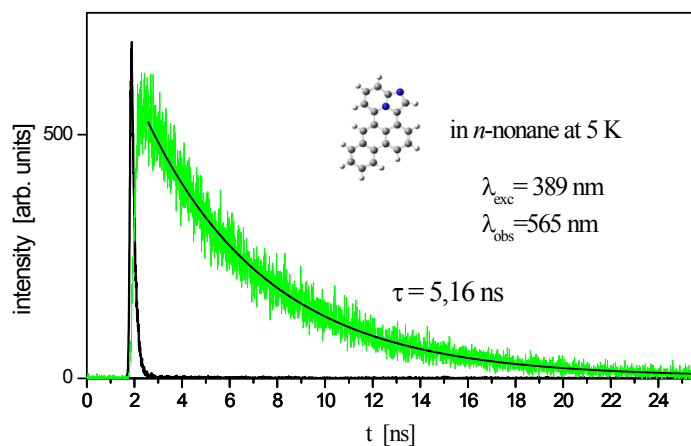


Figure S1. Fluorescence decays of compounds **2** and **3** in *n*-nonane at room temperature (red lines) and at 5 K (green lines). Excitation pulses are given as solid black lines. Fits to the single exponential dependences.

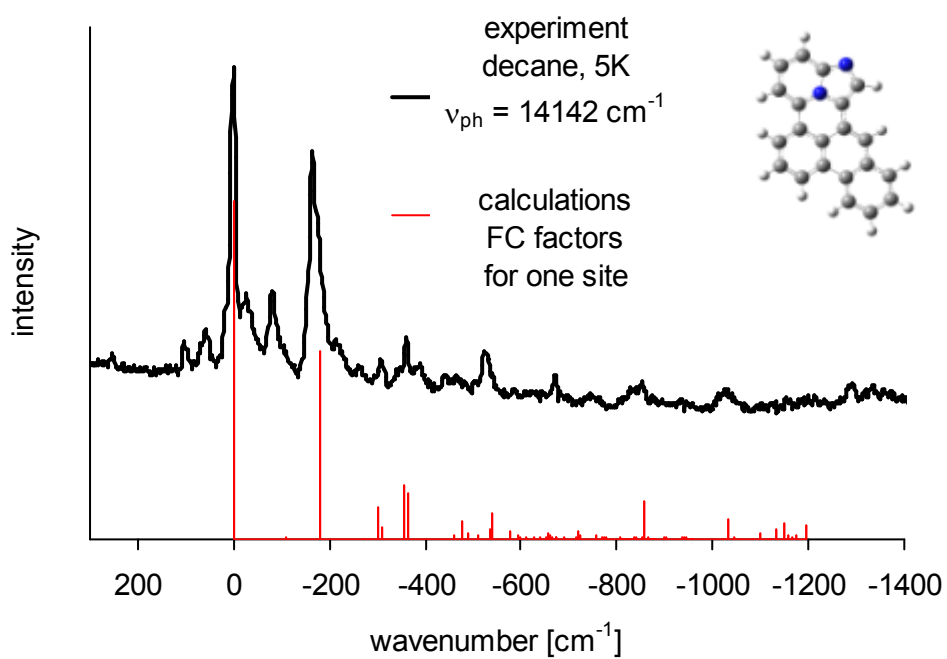


Figure S2. Phosphorescence spectrum of compound **2** in *n*-decane at 5 K, and the calculated Franck-Condon factors (for a single site).

## References

Gaussian 09, Revision B.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J.; Gaussian Inc., Wallingford CT, **2010**.