Electronic Supporting Information

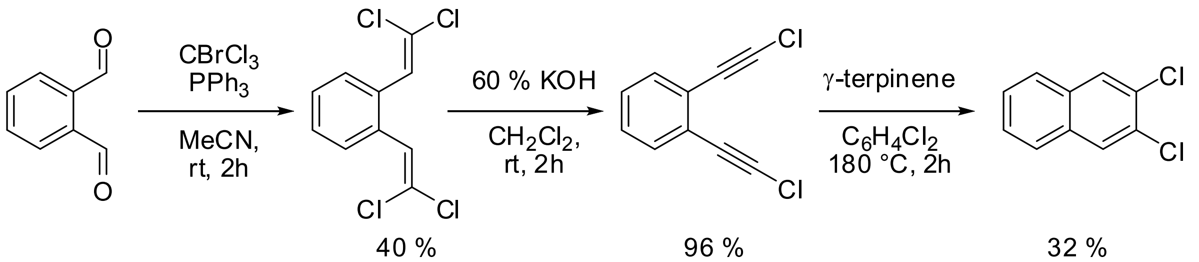
Single molecules of terrylene in di-substituted naphthalenes crystallizing in the herringbone pattern

Magda Białkowska, Wojciech Chaładaj, Irena Deperasińska, Aleksandra Drzewiecka-Antonik, Anna E. Koziol, Artur Makarewicz and Bolesław Kozankiewicz*

1. Synthesis of 2,3-dichloronaphthalene (2,3-DCN) and 2,3-dibromonaphthalene (2,3-DBN).

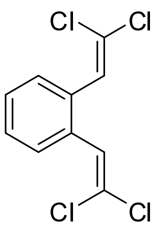
Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates and visualized with UV or cerium molybdate stain (Hanessian's stain). ^{1}H, and ^{13}C{1H} spectra were recorded with a Bruker AV 400 spectrometer. ^{1}H and ^{13}C chemical shifts are given in ppm relative to TMS. The solvent signals were used as references ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.0 ppm) and the chemical shift converted to the TMS scale. Coupling constants (J) are reported in Hz, and the following abbreviations were used to denote multiplets: s = singlet, m = multiplet (denotes complex pattern). Electron ionization high-resolution mass spectra (EI-HR) were recorded with an Autospec Premier (Waters Inc.) mass spectrometer using the narrow-range high-voltage scan technique with low-boiling perfluorokerosene (PFK) as internal standard. Samples were introduced by using a heated direct insertion probe. Unless otherwise noted, all commercially available compounds were used as received.

Synthesis of 2,3-dichloronaphthalene was performed in three steps starting from *o*-phthaladehyde.



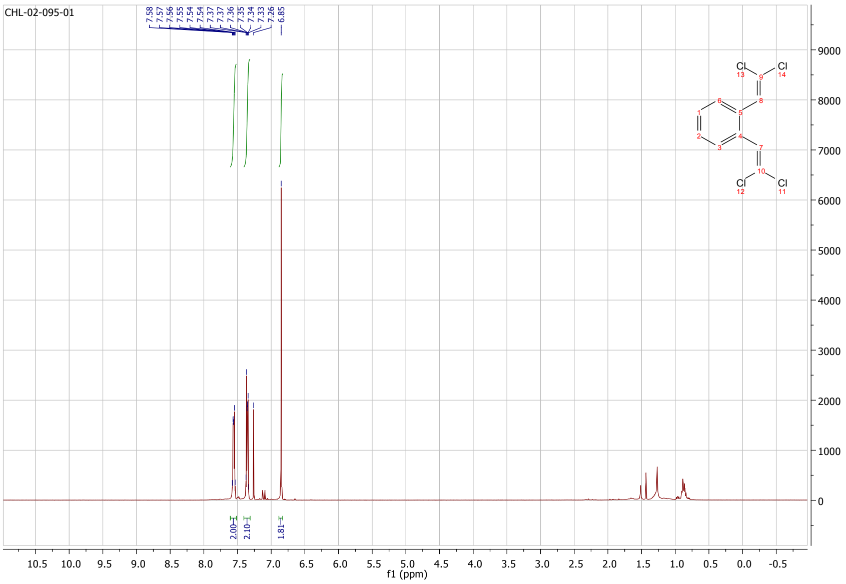
2,3-Dibromonaphthalene was obtained in analog way. 1,2-Bis(bromoethynyl)benzene was obtained from o-phtalaldehyde in two steps, following literature procedure.[3] Bergmann cyclization leading to 2,3-DBN was carried out in similar way and with similar efficiency as for 2,3-DCN. Analytical data for 2,3-DBN were in accordance with literature.[4]

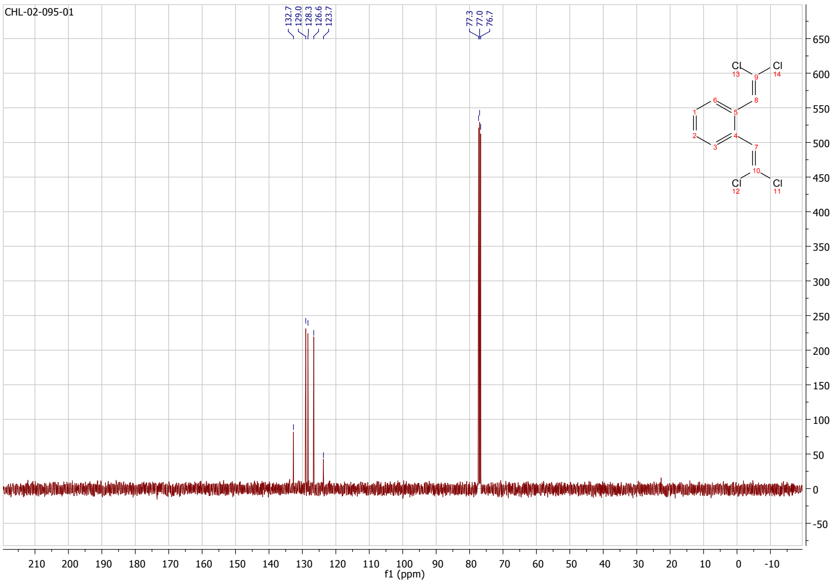
The intermediate compounds were obtained as follows:

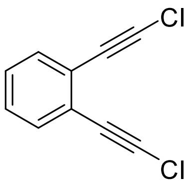


1,2-bis(2,2-dichlorovinyl)benzene. Obtained by adaptation of the procedure developed by Lautens.[1] A solution of o-phthalaldehyde (20.1g, 150 mmol) and PPh_3 (236 g, 900 mmol) in acetonitrile (1.5 L) was placed in an ice-water bath. Then, $CBrCl_3$ (96.8g, 488 mmol) was added to the solution and the stirred reaction mixture was allowed to reach the room temperature. It was stirred until the aldehyde and phosphine was consumed (*ca* 2h, by TLC). The mixture was diluted with a Et_2O–hexanes mixture (3:1) until the solid Ph_3PO began to precipitate. The heterogeneous mixture was then filtered through a pad of silica gel, which was rinsed with a Et_2O–hexanes mixture (3:1). The crude product was purified by short column chromatography (100 g of silica, hexanes) yielding desired product as a colorless oil (15.9 g, 59.3 mmol, 40 %). The material was used without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.38 – 7.32 (m, 2H), 6.85 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 129.0, 128.3, 126.6, 123.7.

1H and 13C{1H} NMR spectra of the isolated compound.

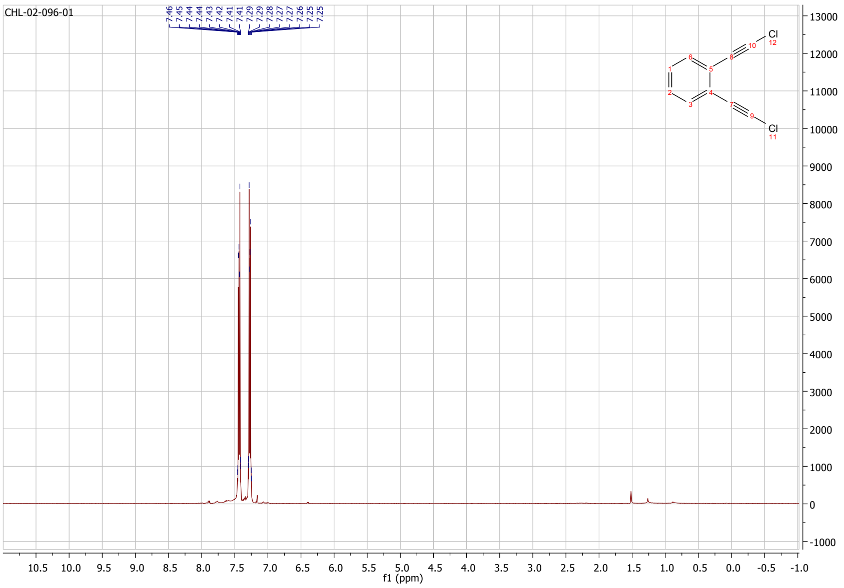


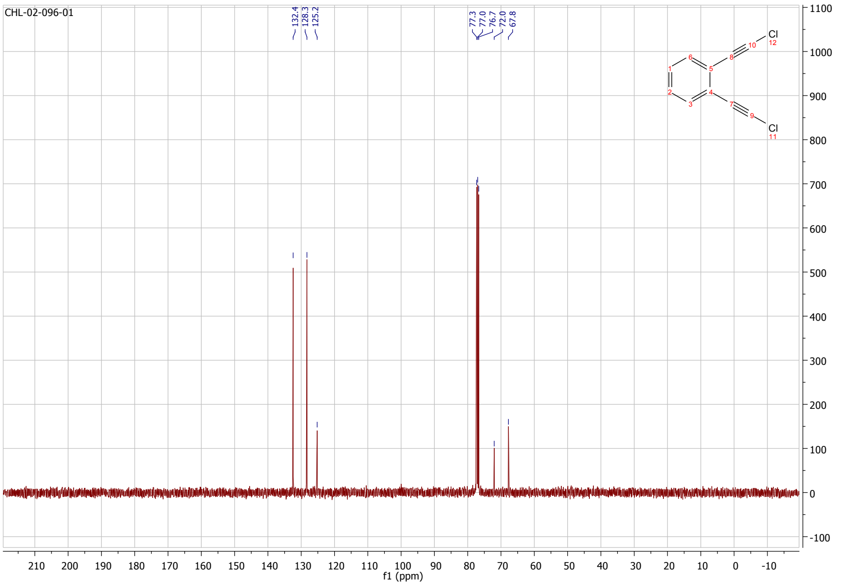


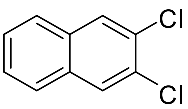


1,2-bis(chloroethynyl)benzene. A solution of 1,2-bis(2,2-dichlorovinyl) benzene (15 g, 56.0 mmol) and tetrabutylammonium chloride (5 mol%) in CH_2Cl_2 (50 mL) was vigorously stirred with 60% aquas KOH (50 mL) for 2h. Then the phases were separated and the aquas phase was extracted with MTBE (2×50 ml). Combined organic phases were washed with saturated NH_4Cl, dried (Na_2SO_4) and concentrated. The crude product was purified by passing through a short column of silica gel (~50g of silica, hexanes) yielding the desired product as a colorless oil (10.5 g, 53.7 mmol, 96 %). The material was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.30 – 7.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 128.3, 125.2, 72.0, 67.8.

1H and 13C{1H} NMR spectra of the isolated compound.

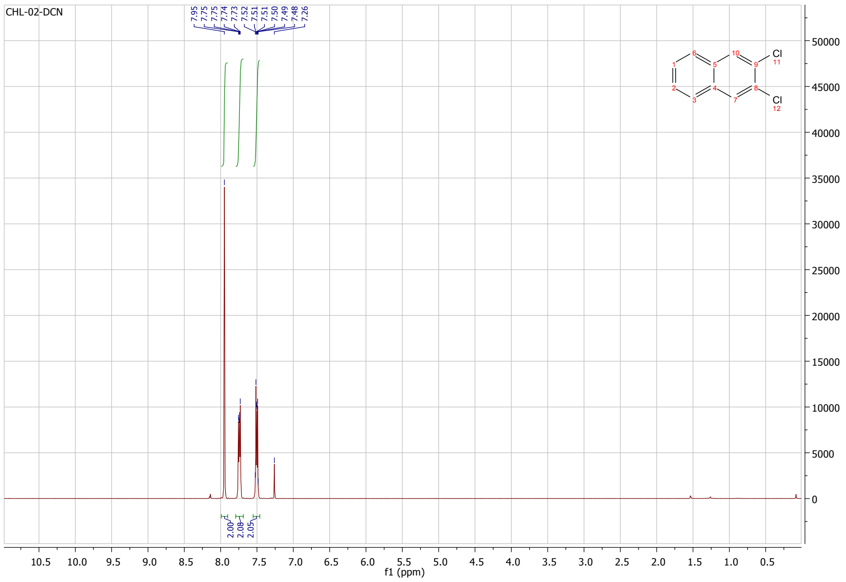


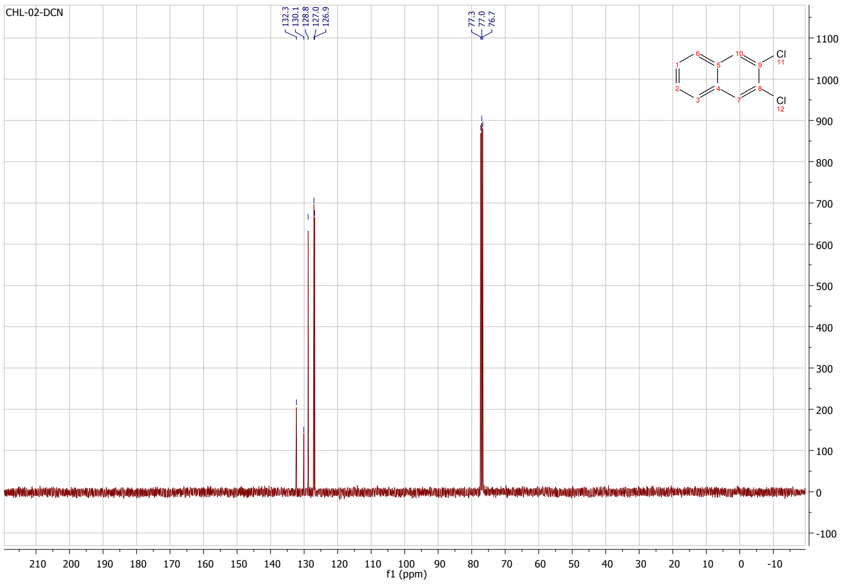




2,3-dichloronaphthalene. Obtained by modified procedure by Anthony.[2] All solutions and solvents used in the reaction were deoxygenated by flushing argon for 20 minutes. A solution of 1,2-bis(chloroethynyl)benzene (10.0 g, mmol 51.3 mmol) in *o*-dichlorobenzene/γ-terpinene (50 ml, 5:1 v/v) was added dropwise over 2h to *o*-dichlorobenzene/ γ-terpinene (300 ml, 5:1 v/v) heated to 180 °C, and the reaction mixture stirred at 180 °C for 2h. Then, solvents were distilled off under reduced pressure and the residue was purified by column chromatography (silica gel ~ 200 g, hexanes). The crude product was purified by sublimation followed by recrystallization from hexanes giving desired product as a white crystals (3.23 g, 16.4 mmol, 32 %). Finally, the material was purified by zone melting technique. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (s, 2H), 7.77 – 7.71 (m, 2H), 7.53 – 7.47 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 132.28, 130.10, 128.80, 127.04, 126.86. MS (EI), *m*/*z* (%): 196 (100, M$^+$), 161 (26), 126 (35), 98 (21), 75 (13), 63 (13); HRMS, *m*/*z*: calc'd for $C_{10}H_6Cl_2$: 195.9847. Found 195.9853.

1H and 13C{1H} NMR spectra of the isolated compound.





1 S. G. Newman, C. S. Bryan, D. Perez, M. Lautens, *Synthesis* 2011, 342–346.

2 D. M. Bowles, G. J. Palmer, C. A. Landis, J. L. Scott, J. E. Anthony, *Tetrahedron*, 2001, **57**, 3753-3760.

3 M. L. G. Borst, R. E. Bulo, D. J. Gibney, Y. Alem, F. J. J. de Kanter, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* 2005, **127**, 16985-16999.

4 D. M. Bowles, J. E. Anthony, *Org. Lett.*, 2000, **2**, 85-87.

2. X-ray structure analysis of 2,3-DCN and 2,3-DBN single crystals. Intermolecular interactions.

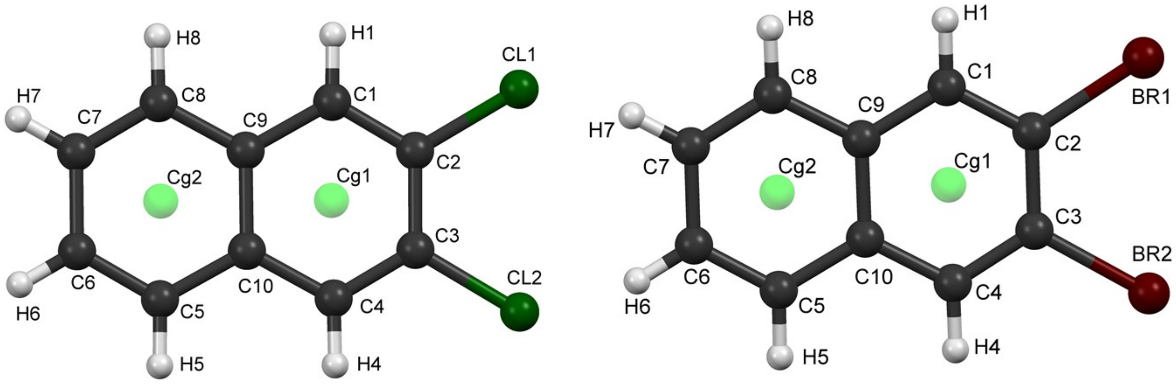


Figure S1. Molecular structure of 2,3-DCN (left) and 2,3-DBN (right) with atom numbering scheme and definition of ring centroids.

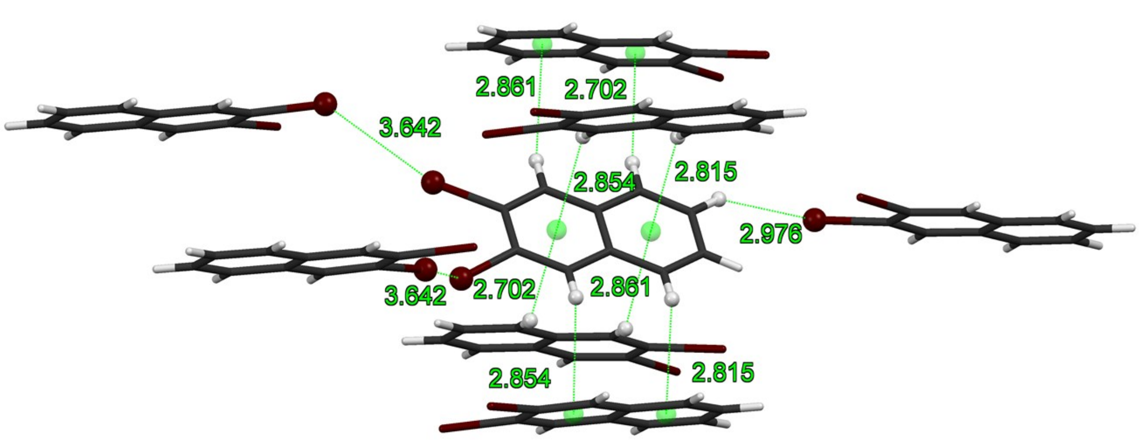


Figure S2. Intermolecular distances in the crystal structure of 2,3-DBN.

Table S1. Geometric parameters of the intermolecular interactions in 2,3-DCN and 2,3-DBN crystals.

(a) C–H···π interactions

Compound	C–H···π	d(H···Cg[a]) [Å]	<C–H···π [°]	d(C···Cg) [Å]
2,3-DCN	C5–H5^{i}···Cg1	2.699	134	3.429
	C4–H4^{i}···Cg2	2.800	134	3.528
	C1–H1···Cg1^{ii}	2.781	134	3.513
	C8–H8···Cg2^{ii}	2.751	134	3.481
	C5–H5···Cg1^{iii}	2.699	134	3.429
	C4–H4···Cg2^{iii}	2.800	134	3.528
	C1–H1^{iv}···Cg1	2.781	134	3.513
	C8–H8^{iv}···Cg2	2.751	134	3.481
2,3-DBN	C5–H5^{v}···Cg1	2.702	135	3.444
	C4–H4^{v}···Cg2	2.861	135	3.598
	C1–H1···Cg1^{vi}	2.854	136	3.603
	C8–H8···Cg2^{vi}	2.815	135	3.549
	C5–H5···Cg1^{vii}	2.702	119	3.444
	C4–H4···Cg2^{vii}	2.861	135	3.598
	C1–H1^{viii}···Cg1	2.854	136	3.603
	C8–H8^{viii}···Cg2	2.815	135	3.549

(b) C–H···halogen interactions

Compound	C–H···Cl/Br	d(H···Cl/Br) [Å]	<C–H···Cl/Br [°]	d(C···Cl/Br) [Å]
2,3-DCN	C6–H6···Cl2^{ix}	2.851	147	3.681
2,3-DBN	C6–H6···Br2^{x}	2.976	150	3.830

(c) halogen···halogen interactions

Compound	X···X	d(X···X)[Å]
2,3-DCN	Cl1···Cl2^{xi}	3.663
	Cl2···Cl1^{xii}	3.663
2,3-DBN	Br1···Br2^{xiii}	3.642
	Br2···Br1^{xiv}	3.642

Symmetry codes: (i) 1-x, 0.5+y, 0.5-z; (ii) 0.5-x, 0.5+y,z; (iii) 1-x, -0.5+y, 0.5-z; (iv) 0.5-x, -0.5+y, z; (v) 1-x,-0.5+y, 0.5-z; (vi) 1.5-x,-0.5+y,z; (vii) 1-x,0.5+y, 0.5-z; (viii) 1.5-x,0.5+y,z; (ix) x, 0.5-y, -0.5+z; (x) x, 1.5-y, -0.5+z; (xi) 0.5+x, 0.5-y, 1-z; (xii) -0.5+x,0.5-y,1-z;

[a] Cg1 and Cg2 are centroids of the rings C1,C2,C3,C4,C10,C9 and C5,C6,C7,C8,C9,C10, respectively

3. Optical studies

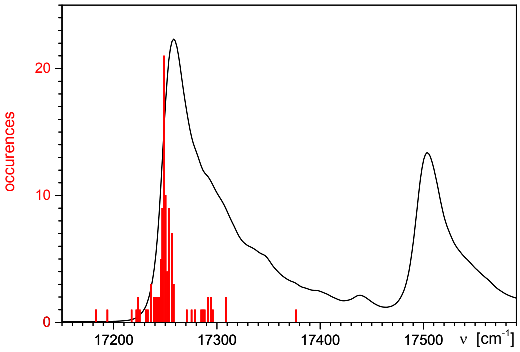


Figure S3. Fluorescence excitation spectrum of an ensemble of Tr molecules in a 2,3-DCN crystal (black line) and the distribution of the purely electronic (0, 0) lines (red).

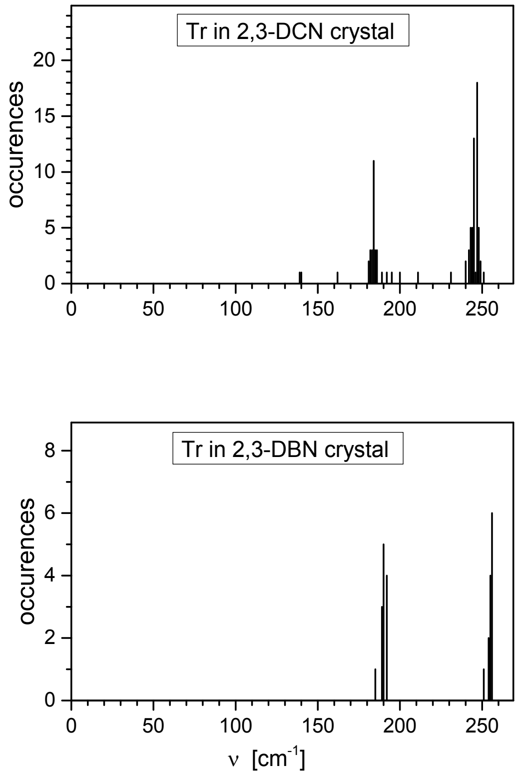


Figure S4. Distribution of the vibronic lines plotted in respect to the purely electronic (0, 0) line of single molecules of Tr in the investigated crystals.

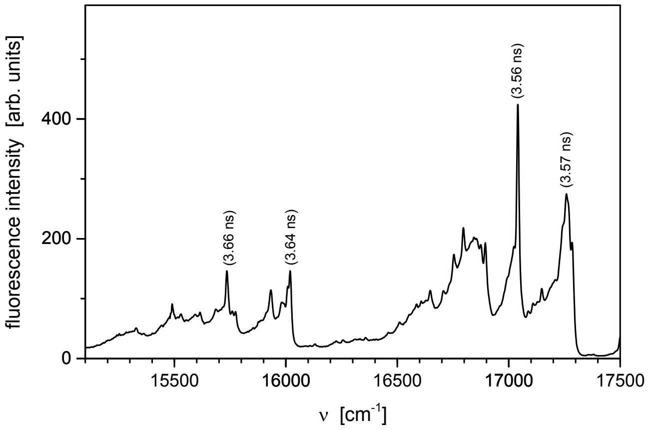


Figure S5. Fluorescence spectrum of a bulk sample of Tr in a 2,3-DBN crystal obtained with λ_{exc}= 532 nm at temperature 5 K. Fluorescence decay times measured with a pulse laser excitation (λ_{exc}= 410 nm) and the observation wavelengths set at different vibrational lines are given in the parentheses.

4. Quantum-chemistry calculations

A. Isolated Tr (D_{2h} symmetry)

Table S2. The coordinates of atoms of isolated Tr molecule optimized in the S_0 and S_1 states.

	S_0 state B3LYP 6-31G(d,p)			S_1 state TD B3LYP 6-31G(d,p)		
	X	Y	Z	X	Y	Z
H	0.000	1.222	6.831	0.000	1.224	6.811
H	0.000	-1.222	6.831	0.000	-1.224	6.811
C	0.000	1.234	5.745	0.000	1.234	5.725
C	0.000	-1.234	5.745	0.000	-1.234	5.725
H	0.000	3.368	5.586	0.000	3.374	5.568
H	0.000	-3.368	5.586	0.000	-3.374	5.568
C	0.000	2.423	5.052	0.000	2.431	5.029

C	0.000	-2.423	5.052	0.000	-2.431	5.029
C	0.000	0.000	5.046	0.000	0.000	5.028
C	0.000	2.427	3.646	0.000	2.441	3.633
C	0.000	-2.427	3.646	0.000	-2.441	3.633
C	0.000	0.000	3.612	0.000	0.000	3.593
H	0.000	3.386	3.143	0.000	3.399	3.128
H	0.000	-3.386	3.143	0.000	-3.399	3.128
C	0.000	1.246	2.907	0.000	1.244	2.886
C	0.000	-1.246	2.907	0.000	-1.244	2.886
C	0.000	1.240	1.435	0.000	1.238	1.435
C	0.000	-1.240	1.435	0.000	-1.238	1.435
H	0.000	3.380	1.198	0.000	3.397	1.198
H	0.000	-3.380	1.198	0.000	-3.397	1.198
C	0.000	0.000	0.720	0.000	0.000	0.720
C	0.000	2.420	0.696	0.000	2.442	0.687
C	0.000	-2.420	0.696	0.000	-2.442	0.687
C	0.000	2.420	-0.696	0.000	2.442	-0.687
C	0.000	-2.420	-0.696	0.000	-2.442	-0.687
C	0.000	0.000	-0.720	0.000	0.000	-0.720
H	0.000	3.380	-1.198	0.000	3.397	-1.198
H	0.000	-3.380	-1.198	0.000	-3.397	-1.198
C	0.000	1.240	-1.435	0.000	1.238	-1.435
C	0.000	-1.240	-1.435	0.000	-1.238	-1.435
C	0.000	1.246	-2.907	0.000	1.244	-2.886
C	0.000	-1.246	-2.907	0.000	-1.244	-2.886
H	0.000	3.386	-3.143	0.000	3.399	-3.128

H	0.000	-3.386	-3.143	0.000	-3.399	-3.128
C	0.000	0.000	-3.612	0.000	0.000	-3.593
C	0.000	2.427	-3.646	0.000	2.441	-3.633
C	0.000	-2.427	-3.646	0.000	-2.441	-3.633
C	0.000	0.000	-5.046	0.000	0.000	-5.028
C	0.000	2.423	-5.052	0.000	2.431	-5.029
C	0.000	-2.423	-5.052	0.000	-2.431	-5.029
H	0.000	3.368	-5.586	0.000	3.374	-5.568
H	0.000	-3.368	-5.586	0.000	-3.374	-5.568
C	0.000	1.234	-5.745	0.000	1.234	-5.725
C	0.000	-1.234	-5.745	0.000	-1.234	-5.725
H	0.000	1.222	-6.831	0.000	1.224	-6.811
H	0.000	-1.222	-6.831	0.000	-1.224	-6.811

Table S3. Vibrational frequencies (given in cm^{-1}) of isolated Tr molecule which geometry was optimized in the S_0 and S_1 states.

No	S_0 state		S_1 state		No	S_0 state		S_1 state		No	S_0 state		S_1 state	
	Sym.	hν	Sym.	hν	no	Sym.	hν	Sym	hν	no	Sym.	hν	Sym	hν
1	A_U	20.7	A_U	27.8	45	A_U	778.9	B_{1G}	759.4	89	B_{2U}	1334.3	A_G	1334.2
2	B_{1G}	28.4	B_{3U}	34.2	46	B_{2G}	780.1	A_U	761.7	90	B_{1U}	1341.6	B_{3G}	1344.2
3	B_{3U}	36.9	B_{1G}	38.3	47	B_{1U}	801.0	B_{3U}	786.5	91	A_G	1343.7	B_{2U}	1363.3
4	B_{2G}	111.6	B_{2G}	107.7	48	A_G	806.8	B_{1G}	787.3	92	B_{3G}	1380.5	A_G	1375.7
5	B_{3U}	112.3	B_{3U}	120.1	49	B_{1U}	814.6	B_{1U}	795.9	93	B_{2U}	1385.5	B_{3G}	1386.2
6	B_{2U}	150.3	B_{2U}	148.4	50	B_{3U}	829.6	A_G	806.0	94	A_G	1391.1	B_{1U}	1387.7
7	B_{2G}	168.3	B_{2G}	173.6	51	B_{1G}	832.4	B_{1U}	810.7	95	B_{1U}	1402.9	B_{2U}	1402.3
8	B_{3U}	181.1	B_{3U}	180.8	52	A_G	838.7	B_{3U}	814.3	96	A_G	1403.2	B_{1U}	1406.7
9	A_U	214.2	A_U	205.6	53	B_{2G}	843.8	B_{2G}	816.0	97	B_{1U}	1414.4	A_G	1409.0

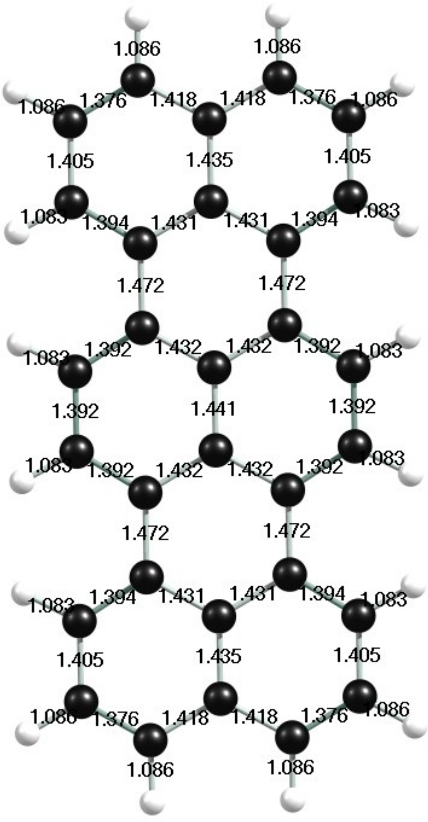
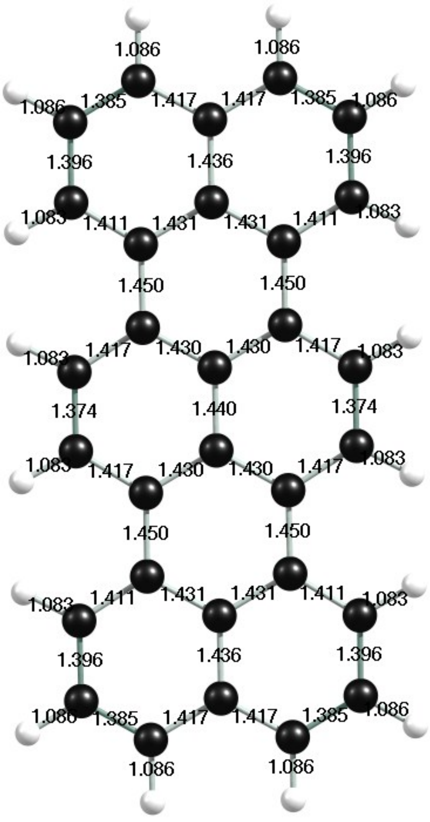
10	B_{1G}	221.0	B_{1G}	214.3	54	B_{3U}	844.2	B2U	828.2	98	B_{1U}	1432.5	B1U	1433.7
11	A_{G}	246.4	A_{G}	247.4	55	B_{2U}	844.3	A_{G}	831.9	99	A_{G}	1454.3	B3G	1439.9
12	B_{3G}	276.9	B_{3U}	273.2	56	A_{U}	884.4	A_{U}	844.0	100	A_{G}	1480.8	A_{G}	1458.3
13	B_{3U}	277.2	B_{3G}	275.6	57	B_{1G}	889.1	B_{1G}	857.8	101	B_{1U}	1491.1	B_{3G}	1478.3
14	A_{U}	297.9	A_{U}	287.2	58	B_{2G}	904.2	B_{2G}	875.6	102	B_{3G}	1494.1	B_{2U}	1481.0
15	B_{2G}	353.3	B_{2G}	337.9	59	B_{3U}	909.3	B_{3U}	887.3	103	B_{3G}	1507.6	A_{G}	1484.0
16	B_{2U}	391.1	B_{2U}	394.5	60	A_{U}	933.5	A_{U}	904.9	104	B_{2U}	1508.9	B_{1U}	1501.7
17	B_{3G}	396.9	B_{3G}	397.5	61	B_{2G}	941.9	B_{2G}	911.5	105	B_{2U}	1551.2	B_{2U}	1534.5
18	B_{1U}	434.6	B_{1G}	409.8	62	B_{1U}	942.4	B_{1U}	943.6	106	B_{3G}	1556.0	B_{3G}	1536.5
19	B_{1G}	435.2	B1U	431.2	63	B_{3G}	965.8	B_{3G}	960.0	107	B_{2U}	1581.2	B_{1U}	1561.1
20	A_{G}	447.9	A_{G}	445.3	64	B_{1G}	970.0	B_{1G}	961.2	108	A_{G}	1605.2	B_{3G}	1590.5
21	B_{2G}	468.4	B_{1U}	475.9	65	A_{U}	971.0	A_{U}	962.5	109	B_{1U}	1622.1	B_{1U}	1594.1
22	B_{3U}	471.4	A_{U}	478.1	66	B_{3U}	979.0	B_{3U}	969.3	110	B_{1U}	1631.4	B_{2U}	1595.1
23	B_{1U}	478.7	B_{3U}	478.7	67	B_{2G}	980.0	B_{2G}	970.4	111	B_{3G}	1637.7	A_{G}	1603.9
24	B_{2G}	481.7	B_{2G}	482.2	68	B_{2U}	1044.5	B_{2U}	1027.3	112	A_{G}	1643.3	B_{1U}	1615.8
25	A_{U}	498.4	B_{2G}	493.3	69	A_{G}	1058.9	A_{G}	1064.1	113	B_{1U}	1643.5	A_{G}	1622.3
26	B_{1U}	528.0	B_{1U}	525.5	70	B_{3G}	1081.0	B_{3G}	1071.3	114	A_{G}	1646.5	A_{G}	1632.0
27	B_{2U}	538.8	B_{2U}	534.1	71	B_{2U}	1093.2	B_{2U}	1100.3	115	B_{2U}	1665.2	B_{2U}	1637.6
28	A_{G}	544.8	A_{G}	541.4	72	A_{G}	1125.5	B_{1U}	1126.4	116	B_{3G}	1668.4	B_{3G}	1637.9
29	B_{3G}	554.1	B_{1G}	546.0	73	B_{1U}	1126.3	A_{G}	1128.0	117	B_{3G}	3180.1	B_{2U}	3179.5
30	B_{3G}	570.5	B_{3G}	550.2	74	B_{3G}	1160.8	B_{3G}	1149.6	118	B_{2U}	3180.2	B_{3G}	3179.8
31	B_{1G}	571.4	B_{3G}	564.0	75	B_{2U}	1173.1	B_{2U}	1167.3	119	B_{1U}	3182.3	B_{1U}	3181.4
32	B_{3U}	579.7	B_{3U}	564.6	76	B_{1U}	1186.0	B_{3G}	1177.9	120	A_{G}	3182.4	A_{G}	3181.8
33	A_{G}	590.1	A_{G}	580.1	77	A_{G}	1186.0	B_{1U}	1185.0	121	B_{3G}	3196.9	B_{3G}	3196.2
34	B_{2G}	628.2	A_{U}	620.1	78	B_{3G}	1198.5	A_{G}	1186.8	122	B_{2U}	3197.4	B_{2U}	3196.4
35	B_{2U}	637.1	B_{2G}	620.8	79	B_{3G}	1218.4	B_{2U}	1208.8	123	B_{1U}	3198.4	B_{1U}	3198.0
36	A_{U}	637.5	B_{2U}	630.2	80	B_{2U}	1222.8	B_{3G}	1209.3	124	A_{G}	3199.2	A_{G}	3198.6

37	B_{1G}	643.8	B_{1G}	631.6	81	B_{1U}	1232.4	B_{1U}	1229.4	125	B_{3G}	3206.6	B_{1U}	3211.3
38	A_{U}	680.8	B_{3U}	671.0	82	B_{2U}	1243.2	B_{2U}	1248.0	126	B_{1U}	3206.8	B_{3G}	3211.5
39	B_{1U}	684.0	A_{U}	672.8	83	A_{G}	1243.6	A_{G}	1248.9	127	B_{2U}	3216.3	B_{2U}	3221.1
40	B_{3U}	703.8	B_{1U}	680.1	84	B_{3G}	1250.3	B_{2U}	1249.7	128	A_{G}	3216.5	A_{G}	3221.4
41	B_{3G}	738.3	B_{2G}	732.3	85	B_{2U}	1256.9	B_{3G}	1253.0	129	B_{3G}	3225.4	B_{3G}	3230.2
42	B_{3U}	765.7	B_{3G}	733.0	86	A_{G}	1307.9	B_{1U}	1301.0	130	B_{1U}	3225.4	B_{1U}	3231.2
43	B_{2G}	772.2	B_{3U}	743.2	87	B_{2U}	1314.3	A_{G}	1315.0	131	B_{2U}	3232.1	B_{2U}	3238.3
44	B_{1G}	774.2	B_{2G}	748.1	88	B_{3G}	1330.9	B_{2U}	1319.8	132	A_{G}	3232.4	A_{G}	3239.2

Table S4. Vibronic frequencies and Franck-Condon factors (intensity) for the $S_0 \rightarrow S_1$ transition calculated for isolated Tr molecule (D_{2h} symmetry).

vibronic state	frequency [cm^{-1}]	intensity
	0	5.69
|11^1>	247	1.32
|20^1>	445	0.05
|11^2>	494	0.15
|28^1>	541	0.35
|33^1>	580	0.17
|28^1;11^1>	788	0.08
|33^1;11^1>	827	0.04
|87^1>	1315	1.66
|91^1>	1363	0.73
|94^1>	1388	0.23
|96^1>	1407	0.13
|87^1;11^1>	1582	0.38
|108^1>	1590	1.27
|91^1;11^1>	1610	0.17
|94^1;11^1>	1635	0.05
|87^1;11^2>	1809	0.04
|108^1;11^1>	1837	0.29
|87^1;28^1>	1856	0.10
|87^1;33^1>	1895	0.05
|91^1;28^1>	1904	0.05

Table S5. Bond lengths in the S_0 and S_1 states of isolated Tr calculated with the 6-31G(d,p).

	S_0	S_1
B3LYP/6-31G(d,p)		

B. Modeling of the deformation of Tr molecule leading to C_{2h}, C_{2v} and D_2 symmetries

Table S6. Coordinates of the atoms in Tr molecule deformed from the planar D_{2h} to lower symmetries by taking deviations in the out-of-plane direction (along the X axis) proportionally to the amplitudes of $7B_{2g}$, $8B_{3u}$ and $9A_u$ vibrations. The starting point in the modeling were the results of DFT and TD DFT B3LYP calculations with 8-31G(d,p) basis obtained for Tr molecule in the D_{2h} symmetry. Coordinates Y and Z were taken the same in all considered cases. Calculated out-of-plane deviations in the excited S_1 state were very small and thus were taken as equal in all cases. All calculated frequencies of vibrations in the provided geometries were positive, the frequencies of 33 lowest energy vibrations are collected in table S7.

	X(D_{2h})	X(C_{2h})	X(C_{2v})	X(D_2)	Y	Z
H	0.000	0.001	0.002	-0.028	1.222	6.831
H	0.000	0.001	0.002	0.028	-1.222	6.831
C	0.000	-0.002	0.004	-0.015	1.234	5.745
C	0.000	-0.002	0.004	0.015	-1.234	5.745
H	0.000	0.030	-0.024	-0.018	3.368	5.586
H	0.000	0.030	-0.024	0.018	-3.368	5.586
C	0.000	0.013	-0.011	-0.009	2.423	5.052
C	0.000	0.013	-0.011	0.009	-2.423	5.052
C	0.000	-0.012	0.011	0.000	0.000	5.046
C	0.000	0.010	-0.009	0.013	2.427	3.646
C	0.000	0.010	-0.009	-0.013	-2.427	3.646
C	0.000	-0.017	0.013	0.000	0.000	3.612
H	0.000	0.027	-0.020	0.024	3.386	3.143
H	0.000	0.027	-0.020	-0.024	-3.386	3.143
C	0.000	-0.010	0.006	0.010	1.246	2.907
C	0.000	-0.010	0.006	-0.010	-1.246	2.907
C	0.000	-0.010	0.007	0.008	1.240	1.435
C	0.000	-0.010	0.007	-0.008	-1.240	1.435
H	0.000	-0.013	-0.028	0.011	3.380	1.198
H	0.000	-0.013	-0.028	-0.011	-3.380	1.198
C	0.000	-0.005	0.017	0.000	0.000	0.720
C	0.000	-0.006	-0.011	0.006	2.420	0.696
C	0.000	-0.006	-0.011	-0.006	-2.420	0.696
C	0.000	0.006	-0.011	0.006	-2.420	-0.696
C	0.000	0.006	-0.011	-0.006	2.420	-0.696
C	0.000	0.005	0.017	0.000	0.000	-0.720

H	0.000	0.013	-0.028	-0.011	3.380	-1.198
H	0.000	0.013	-0.028	0.011	-3.380	-1.198
C	0.000	0.010	0.007	0.008	-1.240	-1.435
C	0.000	0.010	0.007	-0.008	1.240	-1.435
C	0.000	0.010	0.006	0.010	-1.246	-2.907
C	0.000	0.010	0.006	-0.010	1.246	-2.907
H	0.000	-0.027	-0.020	0.024	-3.386	-3.143
H	0.000	-0.027	-0.020	-0.024	3.386	-3.143
C	0.000	0.017	0.013	0.000	0.000	-3.612
C	0.000	-0.010	-0.009	0.013	-2.427	-3.646
C	0.000	-0.010	-0.009	-0.013	2.427	-3.646
C	0.000	0.012	0.011	0.000	0.000	-5.046
C	0.000	-0.013	-0.011	-0.009	-2.423	-5.052
C	0.000	-0.013	-0.011	0.009	2.423	-5.052
H	0.000	-0.030	-0.024	-0.018	-3.368	-5.586
H	0.000	-0.030	-0.024	0.018	3.368	-5.586
C	0.000	0.002	0.004	-0.015	-1.234	-5.745
C	0.000	0.002	0.004	0.015	1.234	-5.745
H	0.000	-0.001	0.002	-0.028	-1.222	-6.831
H	0.000	-0.001	0.002	0.028	1.222	-6.831

Table S7. Frequencies of the 33 lowest energy vibrations in Tr molecule deformed to the lower symmetries, as considered in table S6.

	$D_{2h}(S_0)$		$C_{2h}(S_0)$ (def. $7b_{2g}$)		$C_{2v}(S_0)$ (def. $8b_{3u}$)		$D_2(S_0)$ (def. $9a_u$)		$D_{2h}(S_1)$	
no	symm	freq [cm^{-1}]	symm	freq [cm^{-1}]	symm	freq [cm^{-1}]	symm	freq [cm^{-1}]	symm	freq [cm^{-1}]
1	A_U	20.7	A_U	21.5	A_2	21.1	A	20.9	A_U	27.8
2	B_{1G}	28.4	B_G	29.1	B_1	29.1	B_1	28.5	B_{3U}	34.2
3	B_{3U}	36.9	B_U	37.0	A_1	37.0	B_3	37.2	B_{1G}	38.3
4	B_{2G}	111.6	A_G	111.8	B_2	111.7	B_2	111.9	B_{2G}	107.7
5	B_{3U}	112.3	B_U	112.8	A_1	112.7	B_3	112.5	B_{3U}	120.1
6	B_{2U}	150.3	A_U	150.3	B_1	150.3	B_2	150.3	B_{2U}	148.4
7	B_{2G}	168.3	A_G	168.7	B_2	168.5	B_2	168.4	B_{2G}	173.6
8	B_{3U}	181.1	B_U	181.3	A_1	181.4	B_3	181.1	B_{3U}	180.8
9	A_U	214.2	A_U	214.3	A_2	214.3	A	214.4	A_U	205.6
10	B_{1G}	221.0	B_G	221.1	B_1	221.1	B_1	221.3	B_{1G}	214.3
11	A_G	246.4	A_G	246.3	A_1	246.3	A	246.4	A_G	247.4
12	B_{3G}	276.9	B_G	276.9	A_2	276.9	B_3	275.6	B_{3U}	273.2
13	B_{3U}	277.2	B_U	277.3	A_1	277.3	B_3	278.5	B_{3G}	275.6
14	A_U	297.9	A_U	298.1	A_2	298.0	A	298.0	A_U	287.2
15	B_{2G}	353.3	A_G	353.4	B_2	353.3	B_2	353.3	B_{2G}	337.9
16	B_{2U}	391.1	A_U	391.1	B_1	391.1	B_2	391.1	B_{2U}	394.5
17	B_{3G}	396.9	B_G	396.9	A_2	396.9	B_3	396.9	B_{3G}	397.5
18	B_{1U}	434.6	B_U	434.4	B_2	434.5	B_1	433.7	B_{1G}	409.8
19	B_{1G}	435.2	B_G	435.3	B_1	435.3	B_1	436.1	B_{1U}	431.2

20	A_G	447.9	A_G	447.8	A_1	447.8	A	447.9	A_G	445.3
21	B_{2G}	468.4	A_G	468.6	B_2	468.5	B_2	468.5	B_{1U}	475.9
22	B_{3U}	471.4	B_U	471.6	A_1	471.6	B_3	471.6	A_U	478.1
23	B_{1U}	478.7	B_U	478.8	B_2	478.4	B_1	478.7	B_{3U}	478.7
24	B_{2G}	481.7	A_G	481.8	B_2	482.2	B_2	481.8	B_{2G}	482.2
25	A_U	498.4	A_U	498.5	A_2	498.5	A	498.5	B_{2G}	493.3
26	B_{1U}	528.0	B_U	528.0	B_2	528.1	B_1	528.0	B_{1U}	525.5
27	B_{2U}	538.8	A_U	538.8	B_1	538.8	B_2	538.8	B_{2U}	534.1
28	A_G	544.8	A_G	544.8	A_1	544.8	A	544.8	A_G	541.4
29	B_{3G}	554.1	B_G	554.1	A_2	554.1	B_3	554.1	B_{1G}	546.0
30	B_{3G}	570.5	B_G	570.5	A_2	570.5	B_3	570.5	B_{3G}	550.2
31	B_{1G}	571.4	B_G	571.5	B_1	571.5	B_1	571.4	B_{3G}	564.0
32	B_{3U}	579.7	B_U	579.7	A_1	579.7	B_3	579.8	B_{3U}	564.6
33	A_G	590.1	A_G	590.1	A_1	590.1	A	590.1	A_G	580.1

Table S8. Frequencies (ν) and intensities (I) of additional lines (indicated by bold) in the fluorescence excitation spectrum of Tr molecule deformed to the lower symmetries considered in tables S5 and S7.

D_{2h}			**C_{2h}** (def $7b_{2g}$)			**C_{2v}** (def. $8b_{3u}$)			**D_2** (def.9 $_{au}$)		
vibronic state	ν [cm^{-1}]	I	vibronic state	ν [cm^{-1}]	I	vibronic state	ν [cm^{-1}]	I	vibronic state	ν [cm^{-1}]	I
	0	5.598		0	5.048		0	5.059		0	4.916
			|7^1>	***173.6***	***0.517***						
						|8^1>	***180.8***	***0.579***			
									|9^1>	***205.6***	***0.527***
|11^1>	247.4	2.021	|11^1>	247.4	1.866	|11^1>	247.4	1.824	|11^1>	247.4	1.886
			|7^2>	***347.2***	***0.026***	***|8^2>***	***361.6***	***0.033***	***|9^2>***	***411.2***	0.028
			|11^1;7^1>	***421.0***	***0.191***	***|11^1;8^1>***	***428.2***	***0.209***			
|20^1>	445.3	0.052	|20^1>	445.3	0.052	|20^1>	445.3	0.052	|20^1>	445.3	0.052
									|11^1;9^1>	***453.0***	***0.202***
|11^2>	494.8	0.365	|11^2>	494.8	0.345	|11^2>	494.8	0.329	|11^2>	494.8	0.362
|28^1>	541.4	0.373	|28^1>	541.4	0.314	|28^1>	541.4	0.317	|28^1>	541.4	0.319
|33^1>	580.1	0.208	|33^1>	580.1	0.191	|33^1>	580.1	0.178	|33^1>	580.1	0.179

C. Tr molecule in 2,3-DCN crystal

Table S9. Coordinates of atoms of Tr molecule embedded as dopant in the 2,3-DCN crystal optimized in the S_0 and S_1 states with the aid of ONIOM(STO-3G/UFF) method.

	S_0	STO-3G	UFF		S_1	STO-3G	UFF
H	6.907	1.228	-0.029	H	6.896	1.220	0.023
H	6.900	-1.253	-0.013	H	6.878	-1.264	0.055
C	5.809	1.244	-0.027	C	5.797	1.233	0.021
C	5.802	-1.263	-0.011	C	5.780	-1.268	0.026
H	5.654	3.398	-0.097	H	5.656	3.381	-0.095
H	5.636	-3.418	-0.021	H	5.610	-3.425	-0.107
C	5.112	2.443	-0.061	C	5.099	2.440	-0.030
C	5.100	-2.460	-0.011	C	5.071	-2.470	-0.059
C	5.099	-0.007	-0.011	C	5.085	-0.013	0.031
C	3.690	2.452	-0.030	C	3.688	2.466	-0.002
C	3.677	-2.460	0.014	C	3.661	-2.468	-0.072
C	3.653	-0.002	0.022	C	3.636	0.000	0.038
H	3.170	3.414	-0.051	H	3.176	3.435	-0.035
H	3.161	-3.425	0.021	H	3.135	-3.428	-0.138
C	2.944	1.262	0.041	C	2.924	1.265	0.059
C	2.938	-1.263	0.046	C	2.916	-1.254	0.026
C	1.448	1.267	0.089	C	1.450	1.270	0.072
C	1.444	-1.250	0.056	C	1.447	-1.236	0.079
H	1.220	3.427	0.169	H	1.218	3.399	0.146
H	1.215	-3.407	0.014	H	1.234	-3.452	-0.014
C	0.726	0.010	0.035	C	0.726	0.017	0.049
C	0.704	2.462	0.105	C	0.693	2.489	-0.008
C	0.701	-2.441	-0.001	C	0.693	-2.454	0.083
C	-0.704	-2.433	-0.081	C	-0.689	-2.463	-0.007
C	-0.704	2.467	0.014	C	-0.692	2.484	-0.107
C	-0.725	0.016	-0.045	C	-0.728	0.011	-0.040
H	-1.219	3.435	0.024	H	-1.214	3.423	-0.025
H	-1.235	-3.386	-0.129	H	-1.218	-3.443	-0.181
C	-1.444	-1.241	-0.076	C	-1.447	-1.246	-0.065
C	-1.447	1.273	-0.066	C	-1.451	1.262	-0.094
C	-2.935	-1.257	-0.025	C	-2.918	-1.260	-0.052
C	-2.944	1.267	-0.057	C	-2.923	1.260	-0.046
H	-3.148	-3.416	0.138	H	-3.148	-3.437	-0.035
H	-3.189	3.423	0.032	H	-3.158	3.426	0.044
C	-3.652	0.000	-0.040	C	-3.636	-0.002	-0.022
C	-3.670	-2.454	0.074	C	-3.668	-2.473	-0.021
C	-3.697	2.453	0.001	C	-3.682	2.465	0.025

C	-5.092	-2.460	0.063	C	-5.079	-2.468	0.012
C	-5.099	-0.013	-0.033	C	-5.086	-0.007	0.017
C	-5.119	2.433	0.027	C	-5.093	2.451	0.063
H	-5.625	-3.420	0.110	H	-5.621	-3.424	0.024
H	-5.669	3.377	0.090	H	-5.641	3.403	0.102
C	-5.798	-1.269	-0.024	C	-5.785	-1.262	0.019
C	-5.813	1.234	-0.021	C	-5.793	1.242	0.035
H	-6.895	-1.261	-0.051	H	-6.883	-1.257	0.022
H	-6.912	1.217	-0.020	H	-6.892	1.229	0.039

Table S10. Energies of the (0, 0) transition and frequencies of “a_g” and “b_{2g}” vibrations calculated for Tr guest in 2,3-DCN and 2,3-DBN host crystals with the aid of ONIOM method.

ONIOM			E(0,0)	“a_g“		“b_{2g}”	
high level (for Tr)	low level (for crystal)	crystal	[cm^{-1}]	hν(S_0) [cm^{-1}]	hν(S_1) [cm^{-1}]	hν(S_0) [cm^{-1}]	hν(S_1) [cm^{-1}]
B3LYP /6-31G(d,p)	-	-	17125	246	247	168	174
	UFF	2,3-DCN	17107	251		201	
		2,3-DBN	17121	248		197	
	PM3	2,3-DCN	17061				
		2,3-DBN	17372				
B3LYP /STO-3G	-	-	20880	249	250	174	179
	UFF	2,3-DCN	20871	255	256	180	177
		2,3-DBN	20881	253	253	188	175
	PM3	2,3-DCN	20857				
		2,3-DBN	20925				

Table S11. Frequencies of vibrations in the S_0 and S_1 states calculated with the ONIOM(STO-3G/UFF) method for Tr molecule embedded in 2,3-DCN crystal. The shape of vibration no. 15 indicates that it is stretching along the long axis of Tr with the symmetry "a_g", and the vibration no. 11 is characterized by the symmetry "b_{2g}".

	S_0	S_1
1	8.7	9.2
2	25.5	25.7
3	47.0	47.5
4	103.5	103.1
5	107.7	107.6
6	110.9	112.0
7	122.0	121.7
8	129. 1	128.7
9	134.1	133.0
10	154.7	153.4
11	180.1	176.9
12	187.2	192.2
13	204.7	206.4
14	209.7	211.2
15	255.2	250.7
16	258.1	256.1
17	271.0	265.4
18	284.1	283.0
19	304.7	299.1
20	344.5	330.0
21	390.9	372.2