Electronic Supplementary Information

Substituent effects on fluorescence properties of thiazolo[4,5-*b*]pyrazine derivatives

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1. Transient absorption measurements of 3b and 3c in acetonitrile

Figure S1 shows transient absorption spectra obtained upon 355 nm laser photolysis of **3b** and **3c** in deaerated acetonitrile at 295 K. The lifetimes of the transient signals for **3b** and **3c** were, respectively, 4.8 μs and 2.2 μs, which were shortened on exposing the solution to the air. These observations show that the transient signals are due to triplet manifolds of **3b** and **3c**. The spectral shapes are similar to those obtained in cyclohexane.

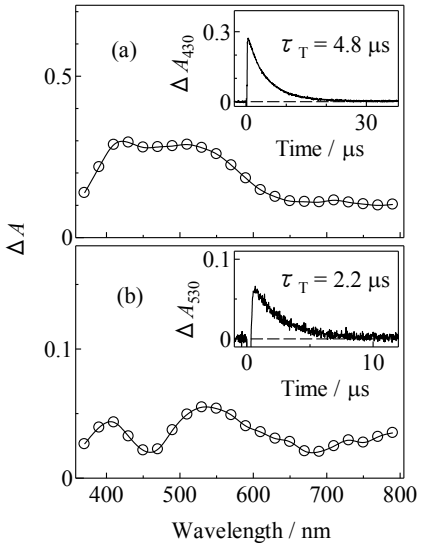

Figure S1. Transient absorption spectra at 600 ns upon 355 nm laser pulsing in acetonitrile solutions of **3b** (a) and **3c** (b) at 295 K. Insets; time profiles at 430 nm (a) and 530 nm (b).

2. Geometries of TPy derivatives in gas phase optimized with DFT using B3LYP/6-31G(d)

2.1 Cartesian coordinates (in Å) of 2-*t*-butylTPy (2)

No	atom	x	y	z
1	H	-4.802612	1.653111	-0.847425
2	C	-4.252591	-0.204774	0.119523
3	C	-3.983874	1.024038	-0.504400
4	N	-2.746112	1.482876	-0.708547
5	C	-1.767169	0.684115	-0.275647
6	C	-2.054893	-0.557606	0.352831
7	N	-3.281714	-1.015491	0.559798
8	N	-0.426724	0.988383	-0.397038
9	C	0.318478	0.054475	0.103063

10	S	-0.555951	-1.348772	0.804483
11	H	-5.276138	-0.540922	0.266667
12	C	1.838724	0.076442	0.048897
13	C	2.456725	-0.753961	1.190166
14	C	2.265037	-0.519704	-1.316859
15	C	2.321139	1.538242	0.146695
16	H	2.156380	-0.373819	2.172703
17	H	2.174381	-1.811820	1.130521
18	H	3.549380	-0.705112	1.128740
19	H	1.843355	0.062632	-2.142209
20	H	3.357845	-0.503141	-1.403473
21	H	1.930844	-1.557995	-1.422240
22	H	3.412558	1.572288	0.052040
23	H	1.878033	2.150753	-0.641774
24	H	2.046385	1.979161	1.111022

2.2 Cartesian coordinates (in Å) of 2-(4-dimethylaminophenyl)TPy (3a)

No	atom	x	y	z
1	H	-1.374926	-2.776492	-1.009406
2	H	4.903706	1.622106	1.157973
3	H	7.311074	1.861506	1.169293
4	H	7.677476	-1.885965	-0.969434
5	H	5.240894	-2.099656	-0.963866
6	C	-1.125598	-0.901440	0.039801
7	C	-0.665600	-2.043407	-0.630329
8	N	0.630268	-2.297554	-0.840341
9	C	1.474801	-1.377980	-0.362646
10	C	0.989468	-0.223030	0.316234
11	N	-0.291460	0.031190	0.525495
12	N	2.839690	-1.465507	-0.482375
13	C	3.434105	-0.441825	0.066501
14	C	4.879154	-0.263577	0.092744
15	C	5.503003	0.846171	0.688223
16	C	6.881462	0.986921	0.696452
17	C	7.717966	0.009798	0.099971
18	C	7.085029	-1.109867	-0.500130
19	C	5.707485	-1.236865	-0.500478
20	S	2.342677	0.779050	0.814197
21	H	-2.189290	-0.733155	0.189260
22	N	9.088844	0.141745	0.102516
23	C	9.921887	-0.877825	-0.514637
24	H	10.970481	-0.595314	-0.409914
25	H	9.785981	-1.858790	-0.038616
26	H	9.705895	-0.987081	-1.586432
27	C	9.709934	1.299030	0.725443
28	H	10.793403	1.224282	0.621373
29	H	9.388653	2.237709	0.252962
30	H	9.476095	1.360474	1.797518

2.3 Cartesian coordinates (in Å) of 2-(4-methoxyphenyl)TPy (3b)

No	atom	x	y	z
1	H	5.952422	1.921039	-0.000549
2	H	-0.906364	-2.130032	-0.000312
3	H	-0.676782	2.164439	0.000438
4	C	5.428539	-0.178666	-0.000594
5	C	5.142272	1.194697	-0.000483
6	N	3.898065	1.682459	-0.000296
7	C	2.927739	0.763310	-0.000220
8	C	3.236077	-0.626535	-0.000344
9	N	4.466651	-1.113164	-0.000524
10	N	1.588842	1.072444	-0.000076
11	C	0.852800	-0.002728	-0.000083
12	C	-0.609284	0.019370	0.000063
13	C	-1.386319	-1.155054	-0.000075
14	C	-2.769826	-1.093074	0.000081
15	C	-3.421498	0.152299	0.000380
16	C	-2.661420	1.332242	0.000505
17	C	-1.272476	1.258037	0.000349
18	S	1.749246	-1.559781	-0.000140
19	H	6.456270	-0.533324	-0.000747
20	C	-5.501323	1.330139	0.001149
21	H	-6.556292	1.051778	0.001426
22	H	-5.281958	1.925426	0.896603
23	H	-5.282587	1.926013	-0.894070
24	O	-4.778270	0.106317	0.000489
25	H	-3.140354	2.304431	0.000697
26	H	-3.374531	-1.993922	-0.000035

2.4 Cartesian coordinates (in Å) of 2-(3,4,5-trimethoxyphenyl)TPy (3c)

No	atom	x	y	z
1	H	6.051741	1.781464	0.248658
2	H	-0.879192	-2.060594	-0.070812
3	H	-0.507241	2.211491	-0.237392
4	C	5.467873	-0.302438	0.219183
5	C	5.222176	1.079066	0.200441
6	N	3.995165	1.602482	0.124819
7	C	3.000524	0.711362	0.066671
8	C	3.267478	-0.686496	0.087008
9	N	4.481372	-1.208691	0.162267
10	N	1.673582	1.058835	-0.014537
11	C	0.907587	0.006051	-0.057706
12	C	-0.553626	0.073330	-0.150241
13	C	-1.344056	-1.085525	-0.151233
14	C	-2.734866	-0.978172	-0.240112
15	C	-3.341044	0.289573	-0.343886
16	C	-2.537041	1.447982	-0.337620
17	C	-1.149568	1.341179	-0.240691
18	S	1.756911	-1.575256	-0.004108

19	H	6.483114	-0.686344	0.281502
20	C	-5.431465	0.767762	0.651236
21	H	-6.481321	0.779082	0.350288
22	H	-5.295083	0.045903	1.466434
23	H	-5.135892	1.767632	0.986504
24	O	-4.693504	0.370829	-0.507905
25	C	-2.458928	3.828424	-0.478576
26	H	-1.879810	3.973232	0.442384
27	H	-1.778258	3.844188	-1.338955
28	H	-3.189475	4.632929	-0.578711
29	O	-3.214137	2.625153	-0.437003
30	C	-3.046244	-3.341439	-0.173416
31	H	-2.393811	-3.546792	-1.032307
32	H	-2.482643	-3.502609	0.755410
33	H	-3.899817	-4.021016	-0.198860
34	O	-3.592781	-2.033659	-0.234810

2.5 Cartesian coordinates (in Å) of 2-phenylTPy (3d)

No	atom	x	y	z
1	H	-1.372746	-2.779102	-1.010240
2	H	4.884872	1.623769	1.159530
3	H	7.336605	1.851476	1.162450
4	H	7.696424	-1.873596	-0.964058
5	H	5.217995	-2.102638	-0.965362
6	C	-1.125065	-0.901983	0.039578
7	C	-0.663986	-2.045764	-0.631309
8	N	0.631007	-2.297803	-0.840129
9	C	1.472608	-1.376382	-0.361585
10	C	0.988536	-0.222727	0.316201
11	N	-0.294114	0.030734	0.525128
12	N	2.839585	-1.461648	-0.480221
13	C	3.427605	-0.438414	0.068459
14	C	4.884689	-0.262014	0.092978
15	C	5.492487	0.853153	0.692551
16	C	6.879408	0.983968	0.695193
17	C	7.677171	0.004341	0.099638
18	C	7.080059	-1.108966	-0.499560
19	C	5.695403	-1.244727	-0.504868
20	S	2.339924	0.779299	0.813918
21	H	-2.189079	-0.735306	0.188163
22	H	8.759181	0.107838	0.102454

2.6 Cartesian coordinates (in Å) of 2-(4-cyanophenyl)TPy (3e)

No	atom	x	y	z
1	H	-4.786066	1.853685	0.000217
2	H	2.134308	-2.079561	0.000289
3	H	4.591974	-1.906371	0.000403
4	H	4.299434	2.391057	-0.000032

5	H	1.814769	2.212602	-0.000128
6	C	-4.227739	-0.239439	0.000545
7	C	-3.963951	1.141339	0.000196
8	N	-2.729251	1.647652	-0.000166
9	C	-1.745451	0.742474	-0.000199
10	C	-2.029511	-0.650561	0.000227
11	N	-3.253255	-1.157698	0.000551
12	N	-0.410416	1.071999	-0.000296
13	C	0.337168	0.006990	0.000008
14	C	1.805442	0.062656	0.000088
15	C	2.597638	-1.097196	0.000228
16	C	3.984090	-1.007854	0.000291
17	C	4.604604	0.252821	0.000198
18	C	3.817525	1.418929	0.000043
19	C	2.433410	1.322340	-0.000013
20	S	-0.529157	-1.559918	-0.000336
21	H	-5.249905	-0.609531	0.000797
22	C	6.034741	0.348923	0.000249
23	N	7.195461	0.426733	0.000290

2.7 Cartesian coordinates (in Å) of 6-(4-dimethylaminophenyl)-2-phenylTPy (4)

No	atom	x	y	z
1	H	-7.563376	-1.420708	-0.426371
2	H	-7.518529	-1.036563	1.309326
3	H	-8.644701	-0.187357	0.230189
4	H	-6.750372	2.361578	0.945530
5	H	-6.736270	2.371341	-0.832376
6	H	-8.189981	1.862708	0.033170
7	H	-5.557293	-2.005001	0.286011
8	H	-3.205415	-2.524024	0.240631
9	H	-2.255786	1.635639	-0.253753
10	H	-4.629488	2.190603	-0.207604
11	H	-1.232728	-2.928447	-0.353507
12	H	4.916324	2.076393	0.186437
13	H	7.366592	2.325186	0.216336
14	H	7.814406	-1.934986	-0.201417
15	H	5.337780	-2.183772	-0.230780
16	N	-6.667895	0.439387	0.024037
17	C	-7.638845	-0.604949	0.303437
18	C	-7.099197	1.827162	0.048523
19	C	-5.317953	0.139687	0.018241
20	C	-4.855129	-1.191653	0.148291
21	C	-3.499220	-1.486306	0.115952
22	C	-2.524711	-0.484422	-0.039767
23	C	-2.985819	0.840609	-0.147319
24	C	-4.335856	1.151361	-0.119784
25	C	-1.080478	-0.771019	-0.079468
26	C	-0.559521	-2.084071	-0.234858
27	N	0.737235	-2.374697	-0.266791
28	C	1.568979	-1.332113	-0.151028

29	C	1.053115	-0.017703	-0.016831
30	N	-0.232484	0.276326	0.022150
31	N	2.938486	-1.438471	-0.161807
32	C	3.505298	-0.272657	-0.044774
33	C	4.960230	-0.078541	-0.024431
34	C	5.543472	1.192912	0.101323
35	C	6.929317	1.335553	0.118235
36	C	7.751698	0.212026	0.009675
37	C	7.179252	-1.057514	-0.116481
38	C	5.796021	-1.205636	-0.133826
39	H	8.832328	0.324750	0.023097
40	S	2.384768	1.124363	0.095203

3. TDDFT calculations for excitations to the first three singlet-excited states of TPy derivatives using B3LYP/6-31G(d)

3.1 Excitation of 2-*t*-butylTPy (2)

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      3.8397 eV  322.90 nm  f=0.0019
      51 -> 52         0.70266

 Excited State   2:      Singlet-A      4.6562 eV  266.28 nm  f=0.0022
      48 -> 52         0.17949
      51 -> 53         0.67768

 Excited State   3:      Singlet-A      4.6930 eV  264.19 nm  f=0.1455
      49 -> 52        -0.26597
      49 -> 53        -0.16365
      50 -> 52         0.61321
      50 -> 53        -0.10065
```

3.2 Excitation of 2-(4-dimethylaminophenyl)TPy (3a)

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      3.4086 eV  363.74 nm  f=0.8154
      67 -> 68         0.70282

 Excited State   2:      Singlet-A      3.7311 eV  332.30 nm  f=0.0013
      66 -> 68         0.69101
      66 -> 69        -0.12428

 Excited State   3:      Singlet-A      4.1127 eV  301.47 nm  f=0.0825
      67 -> 69         0.69161
```

3.3 Excitation of 2-(4-methoxyphenyl)TPy (3b)

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      3.6978 eV  335.29 nm  f=0.0012
      62 -> 64         0.69151
      62 -> 65        -0.12094

 Excited State   2:      Singlet-A      3.7783 eV  328.15 nm  f=0.7651
      63 -> 64         0.69996

 Excited State   3:      Singlet-A      4.4507 eV  278.57 nm  f=0.0159
      59 -> 64         0.13219
      61 -> 64         0.47981
      63 -> 65         0.43396
      63 -> 66         0.19872
```

3.4 Excitation of 2-(3,4,5-trimethoxyphenyl)TPy (3c)

```
Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A      3.5386 eV  350.38 nm  f=0.5313
      78 -> 80         0.13758
      79 -> 80         0.68874

 Excited State   2:      Singlet-A      3.6059 eV  343.84 nm  f=0.0470
      78 -> 80         0.68185
      79 -> 80        -0.13784

 Excited State   3:      Singlet-A      3.6810 eV  336.82 nm  f=0.0013
      77 -> 80         0.68982
      77 -> 81        -0.12018
```

3.5 Excitation of 2-phenylTPy (3d)

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.6421 eV  340.42 nm  f=0.0010
      54 -> 56         0.69141
      54 -> 57        -0.12031

 Excited State   2:      Singlet-A      4.0290 eV  307.73 nm  f=0.6326
      55 -> 56         0.69275

 Excited State   3:      Singlet-A      4.3855 eV  282.71 nm  f=0.0083
      53 -> 56         0.66830
      55 -> 58        -0.17737
```

3.6 Excitation of 2-(4-cyanophenyl)TPy (3e)

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.4791 eV  356.36 nm  f=0.0006
      60 -> 62         0.68539
      60 -> 63         0.14783

 Excited State   2:      Singlet-A      3.8654 eV  320.75 nm  f=0.8124
      61 -> 62         0.69433

 Excited State   3:      Singlet-A      4.3497 eV  285.04 nm  f=0.0306
```

```
      58 -> 62         0.13908
      59 -> 62         0.64726
      61 -> 64         0.18615
```

3.7 Excitation of 6-(4-dimethylaminophenyl)-2-phenylTPy (4)

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      2.9091 eV  426.19 nm  f=0.7736
      87 -> 88         0.70420

 Excited State   2:      Singlet-A      3.5883 eV  345.52 nm  f=0.0010
      85 -> 88         0.69320
      85 -> 89        -0.10692

 Excited State   3:      Singlet-A      3.7297 eV  332.43 nm  f=0.0141
      87 -> 89         0.68986
```