**Supplementary materials**

## Experimental procedures

**General procedure for synthesis of 8.** A solution of salt **7** (17 mmol) in chloroform (150 ml) was shaken with a solution of sodium hydroxide (3.41 g, 85 mmol) in water (40 ml), and an intense yellow color immediately appeared. The organic layer was separated, dried with anhydrous sodium sulfate, and concentrated to give tetrazole-5-aminides **8** as light-yellow crystals. Compound **8a** was crystallized from hexane to give crystals suitable for single crystal X-ray analysis.

**1,3-Di-*tert*-butyltetrazolium-5-aminide (8a).** Yield 3.05 g (91 %). Mp 69–70 °C. UV-Vis, λmax (nm): water – 262; MeOH – 205, 256; CHCl3 – 246, 317; THF – 216, 338; hexane – 224, 344. 1H NMR (500.0 MHz, DMSO-d6), δ: 4.31 (br, s, 1H, NH), 1.59 (s, 9H, t-Bu), 1.54 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 162.1 (CN4), 65.2 (CMe3), 58.9 (CMe3), 28.1 (3Me), 26.5 (3Me) ppm. IR (neat), ṽ: 3327 (w), 3193 (w), 2984 (s), 2941 (s), 2913 (m), 2878 (m), 1610 (s), 1474 (s), 1455 (s), 1420 (m), 1402 (m), 1385 (s), 1369 (s), 1311 (s), 1292 (m), 1175 (s), 1083 (m), 1036 (s), 993 (s), 939 (m), 844 (m), 819 (w), 787 (w), 728 (m), 685 (s), 650 (s), 610 (s), 567 (w), 489 (w), 461 (w), 442 (w), 420 (w) cm–1. Raman, ṽ (rel. int.): 2984 (11), 2928 (21), 2791 (3), 2719 (4), 1620 (14), 1590 (19), 1444 (30), 1403 (54), 1366 (15), 1307 (28), 1288 (5), 1230 (17), 1176 (66), 1149 (16), 1079 (27), 1033 (22), 989 (62), 936 (32), 841 (47), 815 (100), 783 (67), 681 (3), 606 (47), 565 (44), 457 (5), 413 (4), 337 (4), 316 (5), 267 (6) cm–1.

**1-Methyl-3-*tert*-butyltetrazolium-5-aminide (8b).** Yield 2.31 g (88 %). Mp 48–51 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 3.53 (s, 3H, Me), 1.57 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 163.1 (CN4), 66.0 (CMe3), 31.8 (Me), 28.2 (3Me) ppm. IR (neat), ṽ: 3310 (w), 3028 (w), 2991 (m), 2943 (m), 2881 (w), 1824 (w), 1620 (s), 1513 (w), 1462 (s), 1445 (m), 1414 (m), 1373 (s), 1317 (m), 1296 (w), 1223 (s), 1187 (s), 1131 (w), 1100 (w), 1067 (w), 1042 (m), 1006 (w), 988 (m), 943 (w), 934 (w), 843 (s), 736 (s), 675 (s), 589 (m), 570 (m), 513 (w), 460 (w), 438 (w) cm–1.

**3-Methyl-1-*tert*-butyltetrazolium-5-aminide (8c).** Yield 2.53 g (96 %). Mp 44–46 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 4.32 (br, s, 1H, NH), 3.95 (s, 3H, Me), 1.59 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 162.3 (CN4), 59.2 (CMe3), 41.7 (Me), 26.7 (3Me) ppm. IR (neat), ṽ: 3372 (m), 3283 (m), 2979 (w), 2920 (m), 2851 (w), 1741 (w), 1654 (m), 1585 (s), 1484 (w), 1456 (m), 1396 (m), 1356 (s), 1228 (s), 1210 (s), 1163 (s), 1112 (m), 1078 (s), 1039 (m), 1012 (m), 933 (w), 851 (m), 807 (m), 791 (m), 737 (m), 658 (s) cm–1.

**Bistetrazolium salt 9.** To solution of compound **8a** (1.0 g, 5.1 mmol) in acetone (5 ml) 1,2-dibromoethane (0.22 ml, 2.5 mmol) was added. System refluxed 3 h. Precipitate was filtered, dried and washed with cold acetone to give salt **9**. Yield 0.36 g (24 %). Mp 187–190 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 8.01 (s, 1H, NH), 3.65 (s, 4H, 2CH2), 1.70 (s, 9H, t-Bu), 1.67 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 155.5 (CN4), 83.8 (CMe3), 69.1 (CMe3), 64.1 (2CH2), 27.6 (3Me), 26.5 (3Me) ppm. IR (neat), ṽ: 3146 (m), 3100 (m), 2986 (m), 2943 (m), 1622 (s), 1542 (w), 1492 (m), 1437 (w), 1409 (w), 1376 (m), 1352 (m), 1312 (w), 1278 (w), 1242 (m), 1234 (m), 1218 (m), 1187 (s), 1167 (m), 1095 (w), 1073 (w), 1046 (w), 1027 (w), 943 (w), 905 (m), 869 (w), 835 (w), 818 (w), 789 (w), 732 (w), 669 (w), 646 (w), 587 (w), 559 (w), 544 (w), 493 (w), 457 (w), 444 (w), 424 (w) cm–1.

**Bistetrazolium-5-aminide 10.** Compound **9** (0.14 g, 0.33 mmol) was dissolved in chloroform (5 ml), and then a solution of sodium hydroxide (0.132 g, 3.3 mmol) was added. The organic layer was separated, dried with anhydrous sodium sulfate, and concentrated to give **10** as yellow crystals. The obtained compound was recrystallized from toluene to give crystals suitable for single crystal X-ray analysis. Yield 0.10 g (94 %). Mp 192–194 °C. UV-Vis, λmax (nm): MeOH – 206, 263; CHCl3 – 244, 348; THF – 232, 362; hexane – 223, 367. 1H NMR (500.0 MHz, CD3CN), δ: 3.29 (s, 4H, 2CH2), 1.62 (s, 9H, t-Bu), 1.61 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, CD3CN), δ: 158.7 (CN4), 66.9 (CMe3), 60.9 (CMe3), 50.0 (2CH2), 28.3 (3Me), 27.0 (3Me) ppm. IR (neat), ṽ: 2991 (m), 2979 (m), 2965 (m), 2938 (m), 2915 (m), 2874 (m), 2821 (m), 1625 (s), 1479 (m), 1462 (s), 1437 (w), 1397 (m), 1367 (s), 1352 (m), 1290 (s), 1272 (s), 1253 (s), 1211 (w), 1190 (s), 1173 (s), 1116 (s), 1057 (m), 1035 (m), 990 (m), 937 (m), 855 (m), 800 (w), 719 (m), 670 (w), 648 (m), 598 (s), 564 (w), 491 (m), 430 (w) cm–1. Raman, ṽ (rel. int.): 2979 (17), 2926 (24), 2859 (11), 2815 (17), 2715 (5), 1642 (43), 1449 (59), 1403 (73), 1392 (74), 1368 (28), 1345 (10), 1290 (17), 1274 (26), 1263 (26), 1233 (40), 1170 (51), 1109 (56), 1088 (1088), 1030 (38), 986 (74), 929 (38), 866 (21), 815 (100), 802 (36), 714 (4), 649 (66), 609 (6), 562 (44), 470 (11), 450 (10), 371 (3), 340 (9), 267 (5) cm–1.

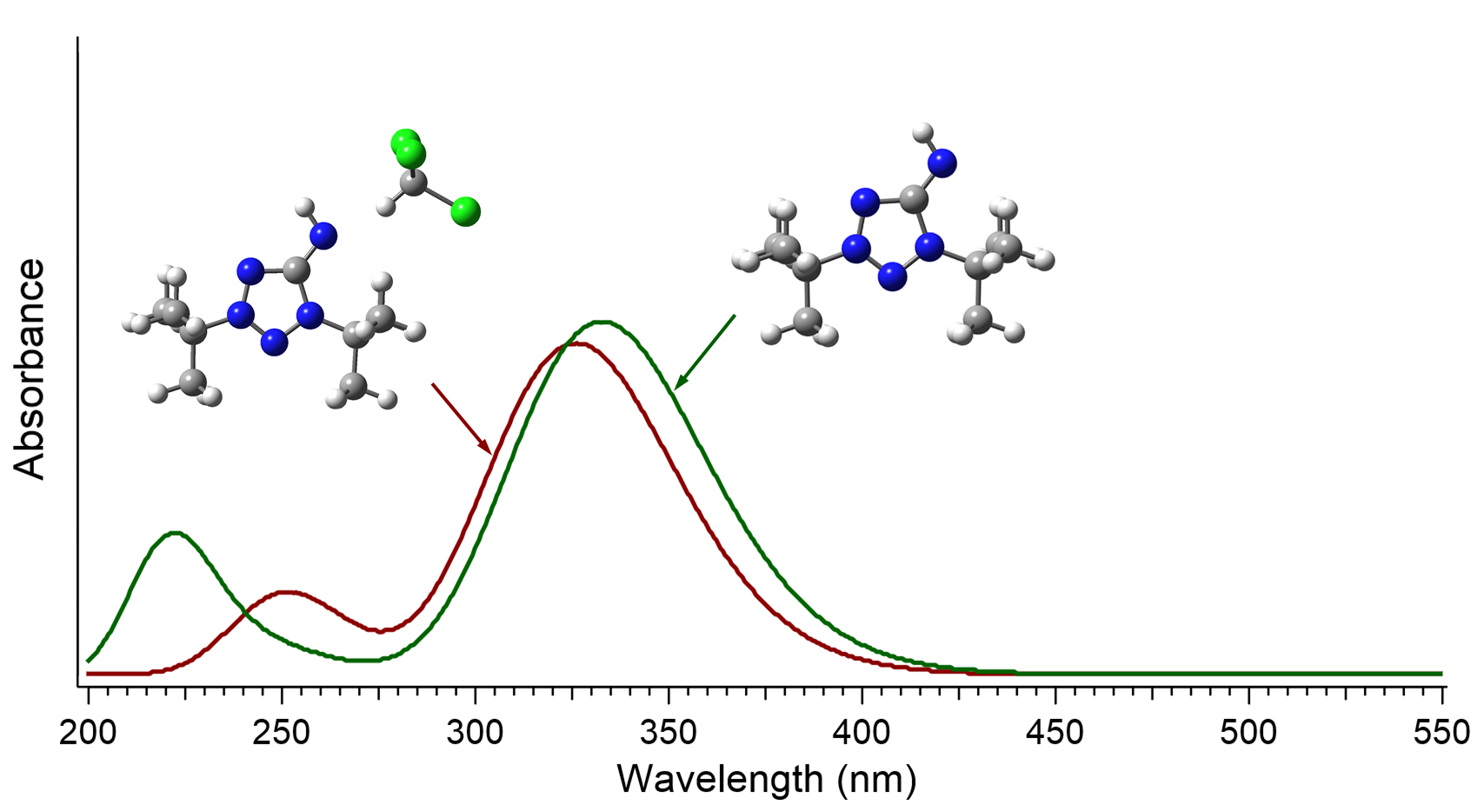
**(1,3-Di-*tert*-butyl-1*H-*tetrazol-3-ium-5-yl)(1-phenyl-1*H*-tetrazol-5-yl)amide (11a).** Compound **8a** (0.43 g, 2.2 mmol) and 5-(methylsulfonyl)-1-phenyl-1H-tetrazole (0.45 g, 2.0 mmol) were dissolved in acetonitrile (10 ml). Sodium hydroxide (0.088 g, 2.2 mmol) was added, and the mixture refluxed for 5 h. Precipitate was filtered and discarded. Filtrate was evaporated to dryness, recrystallized from ethyl alcohol to give **11** as white crystals. After recrystallization from acetonitrile crystals suitable for X-ray analysis were obtained. Yield 0.32 g (46 %). Mp 206–208 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 7.85–7.45 (m, 5H, Ph), 1.69 (s, 9H, t-Bu), 1.70 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 157.9 (CN4), 156.4 (CN4), 135.7 (C4, Ph), 129.6 (C3,5, Ph), 128.4 (C1, Ph), 123.5 (C2,6, Ph), 67.8 (CMe3), 62.6 (CMe3), 28.3 (3Me), 27.1 (3Me) ppm. IR (neat), ṽ: 3363 (w), 3061 (w), 2985 (w), 2667 (w), 2924 (m), 2852 (w), 1603 (m), 1568 (s), 1520 (s), 1499 (s), 1475 (m), 1455 (s), 1412 (m), 1403 (m), 1374 (m), 1363 (m), 1344 (m), 1295 (w), 1276 (w), 1264 (w), 1235 (m), 1213 (m), 1178 (s), 1159 (m), 1124 (m), 1093 (s), 1070 (m), 1044 (w), 1035 (w), 1018 (w), 1002 (m), 984 (w), 969 (w), 962 (w), 938 (w), 912 (m), 868 (m), 839 (w), 827 (w), 816 (w), 758 (s), 745 (m), 739 (m), 694 (m), 686 (s) cm–1.

**N-(2-(*tert*-butyl)-2H-tetrazol-5-yl)-1-phenyl-1H-tetrazol-5-amine (12a).** Compound **11** (0.045 g, 0.13 mmol) refluxed in 2 ml of 10 % HCl for 3 h. After cooling to room temperature precipitate was filtered and recrystallized from ethyl alcohol to give **12** as a white solid. Yield 0,017 g (56 %). Mp 133–135 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 11.06 (br, s, 1H, NH), 7.74–7.53 (m, 5H, Ph), 1.52 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 161.1 (CN4), 151.9 (CN4), 133.8 (C4, Ph), 130.4 (C1, Ph), 130.2 (C2,6, Ph), 124.8 (C3,5, Ph), 64.4 (CMe3), 28.9 (3Me) ppm. IR (neat), ṽ: 2986 (w), 2909 (w), 2828 (w), 2770 (w), 1655 (w), 1615 (s), 1593 (m), 1549 (m), 1524 (s), 1497 (s), 1455 (m), 1402 (w), 1370 (m), 1344 (m), 1314 (m), 1287 (w), 1259 (w), 1237 (w), 1201 (m), 1188 (m), 1172 (w), 1157 (w), 1129 (m), 1093 (m), 1072 (m), 1046 (m), 1012 (s), 988 (w), 939 (w), 918 (w), 861 (m), 831 (m), 814 (w), 760 (s), 748 (s), 722 (s), 685 (s), 595 (m), 554 (m), 503 (w), 476 (w), 449 (w) cm–1.

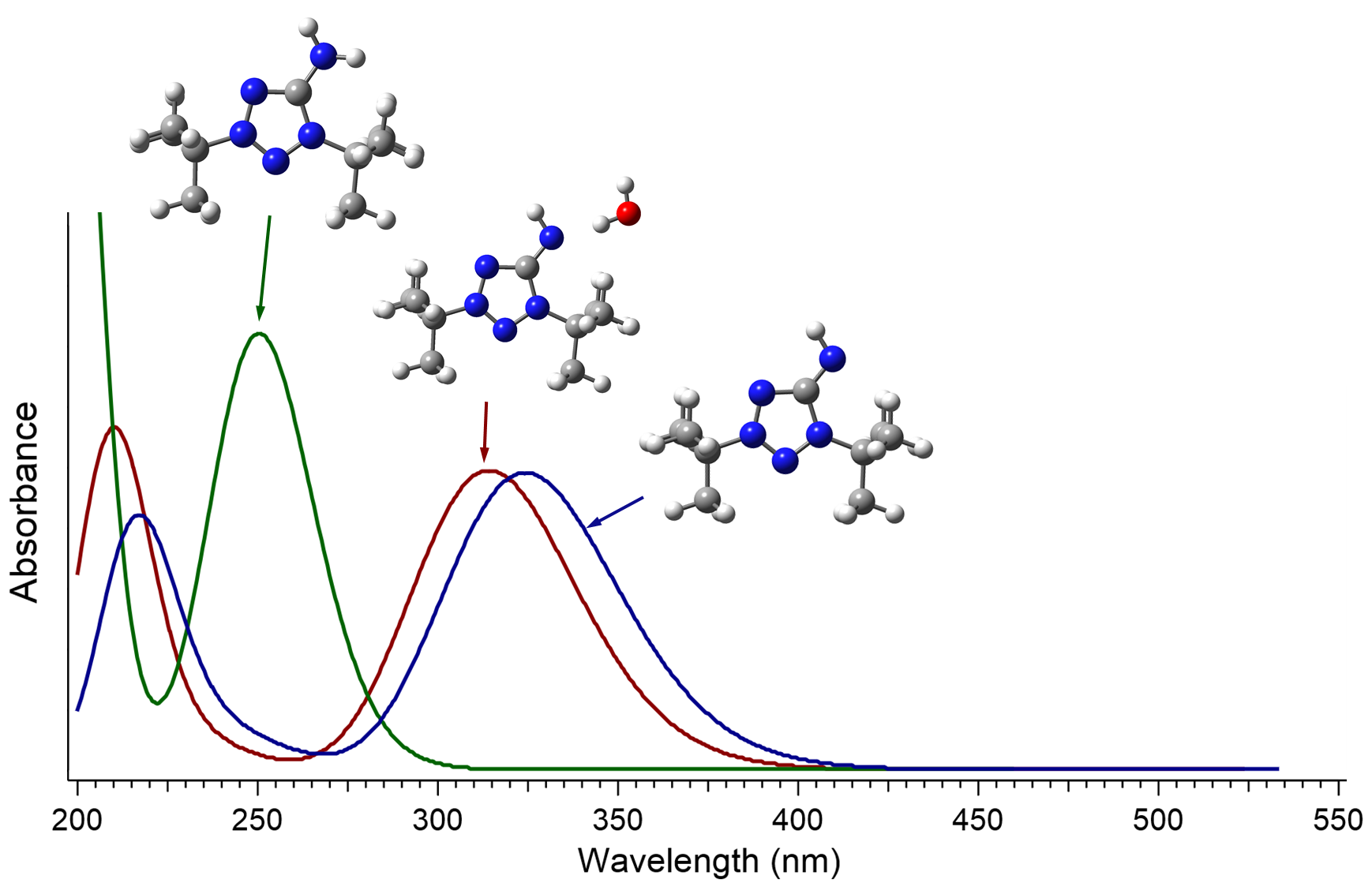
**(1-methyl-3-*tert*-butyl-*1H-*tetrazol-3-ium-5-yl)(1-phenyl-1*H*-tetrazol-5-yl)amide (11b).** Compound **8b** (0.16 g, 1.0 mmol) and 5-(methylsulfonyl)-1-phenyl-1H-tetrazole (0.22 g, 1.0 mmol) were dissolved in acetonitrile (5 ml). Sodium hydroxide (0.044 g, 1.1 mmol) was added and mixture refluxed for 5 h. Precipitate was filtered and discarded. Filtrate was evaporated to dryness, recrystallized from ethyl alcohol to give **13** as white crystals. Yield 0.15 g (50 %). Mp 213–215 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 7.99–7.43 (m, 5H, Ph), 3.84 (s, 3H, Me), 1.70 (s, 9H, t-Bu) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 158.7 (CN4), 156.3 (CN4), 135.8 (C4, Ph), 130.0 (C3,5, Ph), 128.1 (C1, Ph), 122.6 (C2,6, Ph), 68.1 (CMe3), 33.2 (Me), 28.3 (3Me) ppm. IR (neat), ṽ: 3074 (w), 2987 (w), 1652 (w), 1606 (s), 1587 (s), 1525 (s), 1497 (s), 1457 (s), 1414 (w), 1404 (w), 1393 (s), 1375 (s), 1359 (w), 1327 (m), 1292 (m), 1264 (m), 1228 (m), 1182 (s), 1164 (m), 1134 (s), 1099 (s), 1073 (s), 1037 (m), 1017 (m), 987 (s), 925 (m), 900 (s), 824 (w), 764 (s), 743 (w), 729 (m), 696 (m), 666 (s), 616 (w), 576 (m), 546 (m), 542 (m), 518 (w), 491 (m), 468 (m) cm–1.

**1-Methyl-N-(1-phenyl-1*H*-tetrazol-5-yl)-1*H*-tetrazol-5-amine (12b).** Compound **13** (0.1038 g, 0.35 mmol) refluxed in 2.5 ml of 10 % HCl for 6 h. After cooling to room temperature precipitate was filtered and recrystallized from ethyl alcohol to give **12** as a white solid. Yield 0,037 g (44 %). Mp 187–190 °C. 1H NMR (500.0 MHz, DMSO-d6), δ: 7.89–7.50 (m, 5H, Ph), 3.82 (s, 3H, Me) ppm; 13C NMR (125.7 MHz, DMSO-d6), δ: 153.2 (CN4), 151.1 (CN4), 134.4 (C1, Ph), 130.0 (C4, Ph), 129.4 (C2,6, Ph), 123.3 (C3,5, Ph), 32.9 (Me) ppm. IR (neat), ṽ: 3016 (m), 1671 (w), 1623 (s), 1608 (s), 1590 (s), 1537 (s), 1498 (s), 1491 (s), 1450 (s), 1420 (w), 1401 (s), 1328 (w), 1301 (w), 1282 (w), 1268 (w), 1256 (w), 1219 (m), 1175 (w), 1160 (w), 1141 (m), 1115 (s), 1198 (m), 1069 (m), 1023 (s), 1005 (m), 980 (m), 911 (w), 827 (m), 810 (m), 754 (s), 713 (s), 682 (s), 663 (s), 616 (w), 548 (w), 508 (m), 498 (m), 473 (w), 452 (s) cm–1.

**Results of calculations of UV-Vis spectra of 8a**

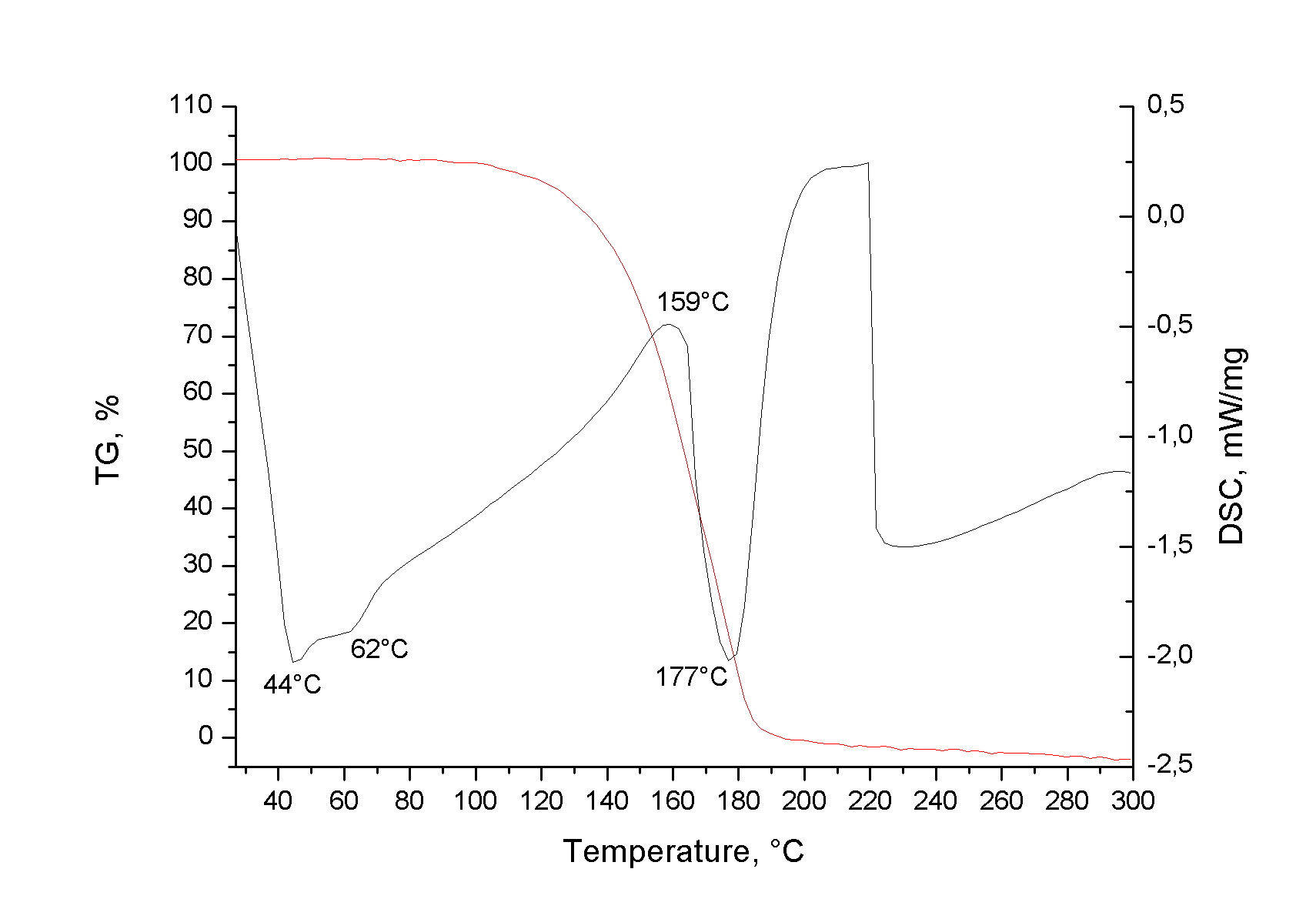


**Fig. S1.** The TD-tHCTHhyb/6-311+G(2d,p) calculated absorption spectra of **8a** in chloroform for two different models: continuum SMD (green curve); combined continuum SMD and super-molecule model, taking into account the formation of a hydrogen bond between **8a** and chloroform (red curve).

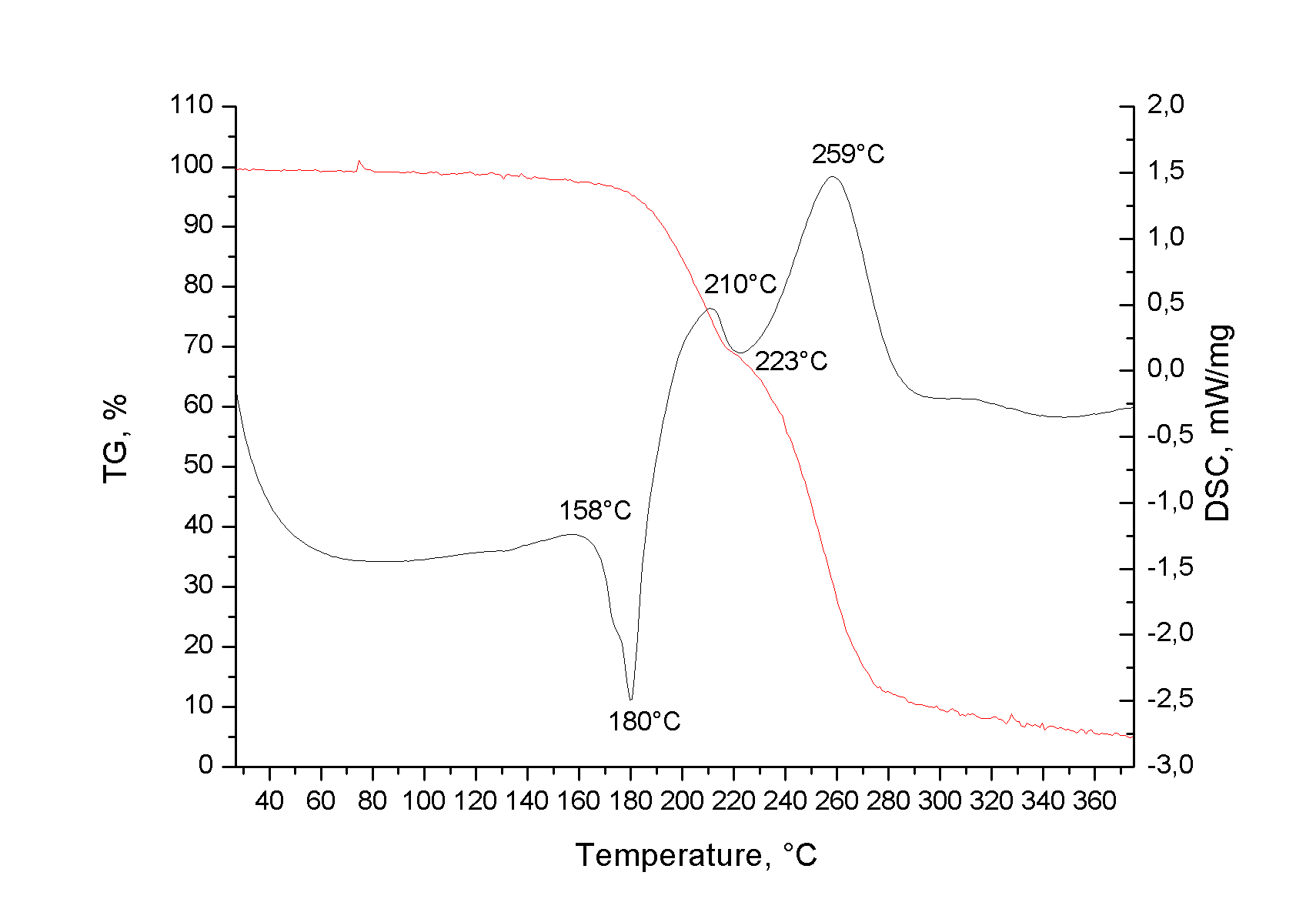


**Fig. S2.** The TD-tHCTHhyb/6-311+G(2d,p) calculated absorption spectra of **8a** in water for three different models: continuum SMD (blue curve); combined continuum SMD and super-molecule model, taking into account the formation of a hydrogen bond between **8a** and chloroform (red curve); continuum SMD model, taking into account the protonation of **8a** in water solution (green curve).

**TGA/DSC details for compounds 8a and 10**



**Fig. S3.** TG and DSC curves of compound **8a**



**Fig. S4.** TG and DSC curves of bistetrazolium-5-aminide **10**