

Supporting Information for

Guanine-Adenine Interactions in DNA Tetranucleotide Cation Radicals Revealed by UV/Vis Photodissociation Action Spectroscopy and Theory

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Table S1. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **G7rA1**.

853.18 (0.0029), 578.85 (0.0233), 551.95 (0.0003), 460.55 (0.0192), 451.47 (0.0013), 426.48 (0.0005), 392.09 (0.0004), 377.13 (0.0015), 371.45 (0.0001), 358.41 (0.0015), 353.00 (0.0008), 351.17 (0.0005), 348.58 (0.0003), 331.43 (0.0017), 329.32 (0.0007), 328.10 (0.0014), 315.45 (0.0003), 313.32 (0.0006), 308.93 (0.0003), 304.22 (0.0007), 301.22 (0.0002), 299.70 (0.0009), 297.22 (0.0127), 295.88 (0.0008), 291.16 (0.0001), 285.63 (0.0008), 282.93 (0.0009), 278.68 (0.0005), 277.92 (0.0002), 274.22 (0.0008), 272.54 (0.0108), 269.07 (0.0000), 265.58 (0.0001), 261.98 (0.0009), 258.87 (0.0012), 256.55 (0.0002), 256.05 (0.0000), 253.98 (0.0004), 252.30 (0.0960), 250.96 (0.0021), 250.06 (0.0053), 249.28 (0.0129), 248.68 (0.0061), 247.39 (0.0208), 245.50 (0.0002), 243.75 (0.0029), 242.25 (0.1940), 241.31 (0.1346), 238.99 (0.0006), 238.06 (0.0005), 237.54 (0.0017), 235.68 (0.0243), 234.57 (0.0029), 234.45 (0.0028), 233.87 (0.0011), 231.40 (0.0005), 230.28 (0.0024), 230.11 (0.0034), 229.73 (0.0029), 227.66 (0.0052), 227.16 (0.0006), 226.36 (0.0007), 226.14 (0.2496), 224.83 (0.0011), 224.75 (0.0059), 224.36 (0.0031), 223.63 (0.0104), 221.56 (0.0089), 221.24 (0.0007), 220.48 (0.0025), 220.22 (0.0028), 219.72 (0.0005), 218.53 (0.0033), 218.01 (0.0024), 217.30 (0.0200), 216.38 (0.0012), 215.03 (0.0008), 214.24 (0.0011), 213.34 (0.0082), 212.23 (0.0029), 211.47 (0.0063), 211.37 (0.0118), 210.89 (0.0023), 210.62 (0.0454), 210.43 (0.0260), 209.36 (0.0072), 209.21 (0.0002), 208.84 (0.0008), 208.62 (0.0034), 208.59 (0.0017).

Table S2. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **rG7A1a**.

651.17 (0.0001), 595.97 (0.0145), 578.13 (0.0047), 460.46 (0.0000), 458.72 (0.0000), 437.42 (0.0017), 400.91 (0.0040), 391.14 (0.0044), 384.03 (0.0114), 370.59 (0.0019), 366.77 (0.0012), 356.74 (0.0002), 344.60 (0.0008), 333.22 (0.0004), 323.30 (0.0059), 317.45 (0.0023), 315.37 (0.0023), 310.78 (0.0002), 307.64 (0.0011), 305.32 (0.0781), 303.89 (0.0011), 300.80 (0.0012), 298.17 (0.0013), 295.19 (0.0008), 294.70 (0.0000), 290.22 (0.0088), 286.70 (0.0411), 283.88 (0.0236), 281.10 (0.0006), 280.27 (0.0034), 277.51 (0.0018), 276.11 (0.0026), 274.04 (0.0007), 269.47 (0.0007), 265.69 (0.0025), 264.11 (0.0004), 261.56 (0.0001), 260.34 (0.0003), 256.06 (0.0008), 255.08 (0.0028), 254.52 (0.0013), 253.62 (0.0003), 250.68 (0.2005), 250.50 (0.0009), 248.34 (0.0005), 247.89 (0.0047), 246.91 (0.0020), 245.05 (0.2151), 243.79 (0.0066), 242.94 (0.0067), 242.87 (0.0012), 242.39 (0.0056), 241.05 (0.0599), 240.70 (0.0027), 240.51 (0.0005), 240.44 (0.0000), 239.37 (0.0531), 238.30 (0.0002), 236.00 (0.0262), 234.01 (0.0992), 233.32 (0.0229), 232.02 (0.0056), 230.67 (0.1568), 229.59 (0.0086), 229.41 (0.0002), 227.63 (0.0003), 226.62 (0.0014), 224.50 (0.0003), 224.45 (0.0010), 222.99 (0.0061), 221.79 (0.0032), 221.38 (0.0001), 220.36 (0.0012), 219.66 (0.0004), 218.91 (0.0040), 218.31 (0.0118), 217.17 (0.0019), 217.00 (0.0001), 215.95 (0.0105), 214.84 (0.0008), 213.96 (0.0006), 213.88 (0.0000), 212.04 (0.0068), 211.76 (0.0000), 211.31 (0.0006), 211.24 (0.0011), 210.24 (0.0155), 209.35 (0.0282), 208.77 (0.0103), 208.63 (0.0002), 208.23 (0.0112), 208.11 (0.0024).

Table S3. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **rG7A1b**.

602.23 (0.0001), 582.03 (0.0000), 548.38 (0.0090), 547.44 (0.0158), 452.09 (0.0021), 429.66 (0.0000), 402.15 (0.0030), 398.55 (0.0014), 390.79 (0.0000), 372.42 (0.0014), 369.79 (0.0098), 368.46 (0.0078), 367.02 (0.0003), 361.16 (0.0059), 355.83 (0.0023), 344.63 (0.0008), 342.14 (0.0041), 327.89 (0.0098), 325.22 (0.0001), 319.58 (0.0046), 316.17 (0.0049), 314.37 (0.0023), 308.66 (0.0312), 306.30 (0.1211), 303.43 (0.0029), 300.29 (0.0008), 297.00 (0.0035), 294.80 (0.0017), 292.13 (0.0055), 291.12 (0.0122), 288.93 (0.0334), 288.29 (0.0052), 283.49 (0.0002), 282.81 (0.0003), 277.14 (0.0001), 276.43 (0.0001), 274.60 (0.0008), 273.07 (0.0001), 273.01 (0.0007), 270.25 (0.0023), 266.88 (0.0000), 266.42 (0.0015), 264.34 (0.0008), 261.41 (0.0009), 259.66 (0.0033), 258.22 (0.0008), 252.84 (0.0011), 252.18 (0.0051), 250.76 (0.0000), 250.56 (0.0035), 249.13 (0.0039), 247.89 (0.0002), 246.86 (0.0023), 245.15 (0.0045), 244.92 (0.0000), 243.44 (0.0007), 242.95 (0.0013), 242.26 (0.0027), 240.64 (0.0000), 239.21 (0.0067), 238.42 (0.0050), 237.88 (0.0006), 237.41 (0.1197), 236.90 (0.0632), 236.57 (0.1388), 236.21 (0.0059), 234.79 (0.0846), 234.15 (0.0021), 234.07 (0.0044), 233.37 (0.0000), 233.05 (0.0057), 232.40 (0.0065), 231.06 (0.3377), 229.99 (0.2292), 228.92 (0.0009), 228.18 (0.0013), 227.01 (0.0010), 225.20 (0.0078), 224.08 (0.0009), 223.56 (0.0013), 222.68 (0.0070), 221.66 (0.0001), 221.09 (0.0057), 220.41 (0.0037), 219.23 (0.0013), 219.07 (0.0095), 218.47 (0.0036), 218.09 (0.0317), 217.63 (0.0149), 216.36 (0.0036), 216.24 (0.0012), 216.07 (0.0009), 214.38 (0.0012), 214.19 (0.0010), 212.95 (0.0018), 212.33 (0.0018), 211.66 (0.0021), 211.60 (0.0032), 209.84 (0.0025), 209.50 (0.0035), 208.71 (0.0003), 208.45 (0.0001), 207.92 (0.0012), 207.80 (0.0003), 207.70 (0.0002).

Table S4. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **G7rT3**.

631.43 (0.0006), 515.32 (0.0039), 451.20 (0.0004), 446.25 (0.0011), 424.74 (0.0000), 375.65 (0.0044), 373.15 (0.0005), 368.23 (0.0030), 364.50 (0.0012), 343.26 (0.0013), 341.76 (0.0004), 335.06 (0.0000), 333.31 (0.0000), 322.03 (0.0017), 320.48 (0.0007), 310.93 (0.0017), 309.26 (0.0061), 306.23 (0.0082), 304.94 (0.0003), 297.72 (0.0014), 292.67 (0.0051), 288.98 (0.0020), 280.42 (0.0069), 279.27 (0.0004), 277.55 (0.0008), 274.81 (0.0013), 272.30 (0.0017), 270.95 (0.0006), 267.42 (0.0032), 265.93 (0.0007), 263.35 (0.0028), 260.45 (0.0010), 256.28 (0.0010), 254.46 (0.0057), 253.70 (0.0035), 253.05 (0.0118), 251.67 (0.0067), 248.30 (0.0014), 247.26 (0.0009), 246.69 (0.0047), 246.38 (0.0906), 245.87 (0.4095), 245.42 (0.0001), 242.93 (0.0437), 242.69 (0.0011), 240.74 (0.0020), 238.92 (0.0130), 238.90 (0.0020), 236.57 (0.0015), 235.90 (0.3438), 235.63 (0.0101), 235.35 (0.0011), 233.56 (0.0106), 231.31 (0.1659), 230.28 (0.0916), 230.04 (0.0028), 229.41 (0.0070), 227.78 (0.0031), 227.43 (0.0001), 224.90 (0.0198), 223.22 (0.0102), 222.06 (0.0004), 221.56 (0.0017), 221.02 (0.0073), 218.95 (0.0007), 218.14 (0.0019), 217.12 (0.0005), 216.13 (0.0036), 215.16 (0.0025), 214.59 (0.0000), 213.52 (0.0007), 213.18 (0.0020), 212.50 (0.0032), 212.15 (0.0000), 211.82 (0.0031), 211.28 (0.0013), 211.02 (0.0002), 209.31 (0.0097), 208.77 (0.0017), 207.65 (0.0026), 207.37 (0.0016), 206.53 (0.0025), 205.44 (0.0019), 204.22 (0.0011), 203.69 (0.0051), 203.61 (0.0030), 203.07 (0.0010), 202.04 (0.0013).

Table S5. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **A1rT3**.

935.13 (0.0000), 820.29 (0.0000), 643.51 (0.0000), 630.21 (0.0000), 617.65 (0.0000), 546.67 (0.0001), 537.69 (0.0001), 513.72 (0.0002), 496.83 (0.0001), 492.76 (0.0029), 468.47 (0.0002), 449.29 (0.0004), 446.74 (0.0001), 421.46 (0.0000), 419.08 (0.0005), 409.90 (0.0001), 399.20 (0.0007), 396.58 (0.0004), 387.47 (0.0066), 383.21 (0.0002), 377.83 (0.0001), 369.03 (0.0008), 366.69 (0.0002), 364.05 (0.0024), 359.83 (0.0008), 351.32 (0.0001), 346.46 (0.0005), 345.43 (0.0034), 334.86 (0.0004), 332.43 (0.0002), 326.96 (0.0003), 324.54 (0.0006), 322.13 (0.0006), 317.13 (0.0019), 311.37 (0.0046), 310.62 (0.0000), 307.87 (0.0007), 306.31 (0.0064), 305.47 (0.0012), 296.48 (0.0031), 294.84 (0.0017), 291.82 (0.0024), 288.89 (0.0034), 286.77 (0.0002), 282.29 (0.0000), 281.72 (0.0005), 281.08 (0.0045), 278.60 (0.0002), 277.33 (0.0006), 273.40 (0.0032), 272.93 (0.0022), 271.04 (0.0000), 270.02 (0.0066), 265.51 (0.0004), 262.88 (0.0081), 260.27 (0.0049), 258.35 (0.0238), 255.04 (0.0063), 253.75 (0.0017), 252.04 (0.0009), 251.81 (0.0000), 250.16 (0.0005), 248.49 (0.2299), 248.46 (0.0001), 245.63 (0.0003), 245.54 (0.0015), 244.95 (0.0128), 243.84 (0.0001), 242.96 (0.0001), 242.92 (0.0001), 242.30 (0.0006), 241.19 (0.0022), 241.08 (0.0016), 240.08 (0.2042), 238.25 (0.0019), 237.99 (0.0396), 237.08 (0.0066), 235.95 (0.0145), 234.13 (0.0009), 232.69 (0.0014), 232.10 (0.0041), 231.75 (0.0001), 230.05 (0.0521), 229.74 (0.0000), 228.75 (0.1499), 228.64 (0.0215), 227.84 (0.0005), 226.75 (0.0886), 226.59 (0.0004), 225.84 (0.0004), 225.37 (0.1510), 224.59 (0.0003), 223.32 (0.0004), 222.50 (0.0000), 222.48 (0.0000), 221.66 (0.0000), 221.06 (0.0053), 220.92 (0.0875), 220.27 (0.0001), 219.73 (0.0098), 219.32 (0.0001), 218.44 (0.0456), 217.72 (0.0042), 217.37 (0.0001), 217.10 (0.0258), 216.93 (0.0016), 214.85 (0.0046), 214.54 (0.0002), 214.34 (0.0014), 213.82 (0.0006), 212.68 (0.0017), 212.62 (0.0004), 211.74 (0.0003), 211.53 (0.0008), 211.43 (0.0010), 210.87 (0.0002), 209.98 (0.0000), 208.43 (0.0000), 208.40 (0.0161), 208.10 (0.0001), 207.20 (0.0004), 206.68 (0.0000), 206.32 (0.0005), 205.97 (0.0013), 205.34 (0.0012), 205.11 (0.0006), 204.57 (0.0008).

Table S6. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **G7rT4**.

729.96 (0.0005), 354.97 (0.0006), 343.18 (0.0033), 334.08 (0.0004), 325.17 (0.0037), 319.55 (0.0217), 304.84 (0.0003), 298.06 (0.0005), 289.60 (0.0011), 287.08 (0.0001), 285.85 (0.0001), 282.49 (0.0014), 280.79 (0.0005), 273.92 (0.0007), 273.34 (0.0045), 271.23 (0.0491), 263.61 (0.0013), 257.64 (0.0083), 255.45 (0.0040), 254.98 (0.0005), 254.74 (0.0001), 250.00 (0.0001), 247.91 (0.0010), 246.90 (0.0088), 241.89 (0.0770), 241.82 (0.0158), 241.65 (0.0595), 239.14 (0.0028), 235.66 (0.0204), 235.19 (0.1923), 233.17 (0.0046), 232.94 (0.0016), 232.32 (0.0961), 232.00 (0.2959), 231.64 (0.0011), 231.01 (0.0008), 229.93 (0.0014), 227.97 (0.0003), 227.18 (0.2461), 226.65 (0.0005), 226.52 (0.0353), 225.14 (0.0016), 221.61 (0.0022), 220.13 (0.0002), 217.27 (0.0015), 215.97 (0.0002), 214.61 (0.0060), 213.74 (0.0012), 213.09 (0.0007), 212.80 (0.0040), 212.72 (0.0031), 211.95 (0.0001), 210.53 (0.0006), 209.85 (0.0018), 206.90 (0.0175), 206.33 (0.0040), 206.04 (0.0008), 205.73 (0.0941), 205.34 (0.0182), 205.32 (0.0067), 204.88 (0.0038), 204.14 (0.0033), 203.96 (0.0001), 203.25 (0.0031), 201.99 (0.0003), 200.80 (0.0193), 200.61 (0.1147), 200.27 (0.0009).

Table S7. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **rG78a**.

380.48 (0.0309), 362.25 (0.0011), 335.25 (0.0756), 324.32 (0.0007), 320.28 (0.0000), 305.78 (0.0002), 298.50 (0.0020), 262.55 (0.1300), 257.37 (0.0016), 255.08 (0.1112), 252.00 (0.0001), 250.74 (0.0025), 248.53 (0.2133), 244.98 (0.0000), 244.56 (0.0000), 244.01 (0.0004), 243.74 (0.0026), 243.32 (0.0061), 241.98 (0.0006), 235.82 (0.2144), 234.30 (0.0011), 232.12 (0.3006), 231.70 (0.0206), 231.34 (0.0013), 230.35 (0.0008), 229.34 (0.0016), 228.94 (0.0027), 226.71 (0.0012), 226.62 (0.0089), 224.81 (0.0232), 223.96 (0.0097), 222.15 (0.0080), 217.57 (0.0007), 217.08 (0.0017), 216.02 (0.0003), 213.58 (0.0068), 213.24 (0.0014), 212.09 (0.0029), 210.09 (0.0001), 209.38 (0.0011), 208.81 (0.0001), 208.74 (0.0050), 206.82 (0.0061), 206.43 (0.0010), 205.86 (0.0005), 204.81 (0.0046), 204.00 (0.0065), 203.81 (0.0381), 203.42 (0.0038), 202.87 (0.0074), 202.33 (0.0805), 201.51 (0.0375), 200.94 (0.0175), 200.83 (0.0568), 200.67 (0.0015), 200.48 (0.0048), 200.09 (0.0002).

Table S8. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **G7rA8**.

418.02 (0.0195), 389.30 (0.0036), 345.25 (0.0068), 315.18 (0.0585), 298.46 (0.0417), 292.27 (0.0665), 266.90 (0.0000), 261.17 (0.0001), 260.40 (0.0000), 252.32 (0.0001), 251.83 (0.0004), 249.47 (0.2332), 248.34 (0.0163), 247.67 (0.0005), 245.43 (0.0342), 244.31 (0.0001), 244.05 (0.0000), 243.14 (0.0958), 241.74 (0.0038), 238.70 (0.0072), 235.14 (0.0003), 234.72 (0.0056), 233.24 (0.0018), 232.07 (0.0009), 231.75 (0.3107), 231.26 (0.0209), 226.35 (0.0018), 225.91 (0.3054), 224.27 (0.0055), 222.52 (0.0048), 221.59 (0.0026), 220.38 (0.0101), 220.06 (0.0284), 217.37 (0.0005), 213.66 (0.0019), 210.60 (0.0034), 209.61 (0.0004), 208.86 (0.0007), 208.52 (0.0006), 207.03 (0.0003), 206.58 (0.0038), 206.39 (0.0019), 204.88 (0.0002), 204.78 (0.0003), 203.76 (0.0058).

Table S9. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **rG78b**.

416.18 (0.0006), 394.11 (0.0411), 344.18 (0.0002), 330.16 (0.0671), 326.19 (0.0036), 298.43 (0.0152), 282.79 (0.0141), 278.86 (0.0146), 278.25 (0.0184), 273.75 (0.0359), 262.71 (0.0160), 262.05 (0.1005), 260.72 (0.0206), 256.24 (0.0411), 253.19 (0.0018), 252.21 (0.0003), 251.25 (0.0027), 249.86 (0.0020), 249.41 (0.0008), 248.25 (0.0037), 246.80 (0.0003), 243.20 (0.1477), 242.32 (0.1461), 240.56 (0.0013), 237.14 (0.0009), 233.96 (0.0129), 233.66 (0.0032), 232.64 (0.2577), 232.24 (0.0306), 231.99 (0.0012), 231.68 (0.0010), 230.35 (0.0033), 228.39 (0.0106), 226.88 (0.0199), 225.98 (0.0024), 225.17 (0.0043), 223.34 (0.0012), 222.76 (0.0021), 221.20 (0.0019), 220.65 (0.0018), 216.88 (0.0044), 214.62 (0.0008), 213.41 (0.0017), 213.39 (0.0015), 213.29 (0.0031), 212.83 (0.0041), 212.70 (0.0003), 210.16 (0.0007), 208.88 (0.0002), 208.22 (0.0023), 207.84 (0.0004), 206.70 (0.0005), 205.68 (0.0055), 205.50 (0.0002), 204.46 (0.0009), 204.20 (0.0075), 204.09 (0.0093), 204.03 (0.0198), 202.75 (0.0164), 202.58 (0.0054), 202.19 (0.0113), 201.45 (0.2159), 200.38 (0.0015), 200.33 (0.0004), 200.09 (0.0003), 200.02 (0.0008).

Table S10. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **rG78c**.

466.47 (0.0004), 403.54 (0.0001), 392.45 (0.0007), 391.63 (0.0521), 361.01 (0.0000), 330.75 (0.0188), 311.22 (0.0003), 303.35 (0.0242), 299.16 (0.0112), 297.42 (0.0272), 283.62 (0.0013), 278.87 (0.0471), 267.85 (0.0007), 267.59 (0.0108), 264.46 (0.0323), 263.00 (0.0007), 260.00 (0.0004), 254.55 (0.0422), 251.01 (0.0016), 250.18 (0.1531), 248.77 (0.0046), 247.99 (0.0108), 247.42 (0.0971), 244.23 (0.0040), 243.85 (0.0031), 243.55 (0.0054), 242.14 (0.0831), 241.88 (0.0165), 240.26 (0.0022), 239.23 (0.1074), 235.53 (0.0011), 234.67 (0.0007), 233.99 (0.0003), 233.28 (0.1949), 230.03 (0.0041), 229.34 (0.0016), 228.39 (0.0035), 227.36 (0.0010), 227.34 (0.0012), 226.50 (0.0070), 226.22 (0.0004), 223.93 (0.0003), 221.87 (0.0142), 221.40 (0.0005), 220.63 (0.0006), 219.95 (0.0010), 219.72 (0.0029), 219.32 (0.0006), 218.65 (0.0059), 218.12 (0.0113), 217.02 (0.0000), 215.76 (0.0000), 210.67 (0.0104), 210.57 (0.0009), 209.90 (0.0081), 209.79 (0.0029), 209.02 (0.0017), 208.83 (0.0097), 208.50 (0.0275), 208.33 (0.0096), 207.63 (0.0007), 207.61 (0.0003), 207.19 (0.0019), 206.92 (0.0058), 206.88 (0.0007), 206.48 (0.0036), 205.79 (0.0009), 205.54 (0.0001), 204.73 (0.0029), 204.23 (0.0036), 202.69 (0.0004), 201.82 (0.0012), 201.72 (0.0025), 201.46 (0.0255), 201.11 (0.0123), 200.84 (0.0101), 200.27 (0.0870).

Table S11. M06-2X/6-31+G(d,p) calculated excitation wavelengths (nm) and oscillator strength (in parentheses) for **rA78**.

474.34 (0.0010), 448.44 (0.0284), 398.05 (0.0022), 367.78 (0.0104), 323.23 (0.0517), 312.28 (0.0108), 293.46 (0.1621), 280.14 (0.0010), 279.25 (0.0114), 269.57 (0.0003), 267.58 (0.0019), 265.92 (0.0007), 263.12 (0.0003), 260.20 (0.0015), 259.21 (0.0009), 254.49 (0.0009), 250.63 (0.0003), 250.41 (0.0003), 248.93 (0.0009), 247.64 (0.0720), 246.04 (0.0026), 245.82 (0.1002), 245.23 (0.0289), 243.77 (0.0000), 243.54 (0.0042), 243.45 (0.0007), 243.06 (0.1978), 242.07 (0.0038), 238.79 (0.1186), 236.89 (0.0032), 236.68 (0.0138), 234.95 (0.0012), 234.63 (0.0041), 232.70 (0.0009), 232.63 (0.0016), 231.43 (0.0008), 230.33 (0.0058), 227.61 (0.0216), 227.10 (0.0003), 225.63 (0.0007), 224.68 (0.0035), 223.80 (0.0929), 222.96 (0.0014), 221.72 (0.0067), 220.88 (0.0157), 220.13 (0.0666), 219.81 (0.0899), 216.83 (0.0020), 216.46 (0.0054), 215.16 (0.0003), 214.89 (0.0057), 214.50 (0.0006), 213.99 (0.0073), 213.40 (0.0017), 212.25 (0.0216), 211.18 (0.0119), 209.33 (0.0054), 209.06 (0.0083), 208.88 (0.0008), 207.11 (0.0768), 207.04 (0.0038), 206.94 (0.0008), 206.73 (0.0243), 206.39 (0.0066), 205.68 (0.0053), 205.26 (0.0003), 204.75 (0.0158), 203.46 (0.0016), 203.00 (0.0555), 201.74 (0.0078), 201.51 (0.0050), 201.32 (0.0979), 200.91 (0.0271), 200.56 (0.0177), 200.25 (0.0004), 200.21 (0.0102).

Table S12. Calculated total and recombination energies of protonated DNA nucleobases.

Species	Energy ^a				
	B3LYP 6-31+G(d,p)	ZPVE ^b	M06-2X 6-31+G(d,p)	M06-2X ^c 6-31++G(2d,p)	CCSD(T) ^{c,d} CBS
Adenine-N-1-H ⁺	−467.724170	329.8	−467.534187	−467.652321	−467.131484
Adenine-N-1-H [•]	−467.888374	318.7	−467.696672	−467.815835	−467.294236
Guanine-N-7-H ⁺	−542.968650	341.3	−542.751844	−542.894554	−542.315853
Guanine-N-7-H [•]	−543.134895	331.3	−542.913537	−543.058757	−542.478326
Cytosine-N-3-H ⁺	−395.339050	295.2	−395.168685	−395.274671	−394.858909
Cytosine-N-3-H [•]	−395.528648	283.1	−395.356707	−395.464292	−395.047311
Thymine-O-4-H ⁺	−454.510897	334.6	−454.317138	−454.442311	−453.973843
Thymine-O-4-H [•]	−454.710370	320.2	−454.515429	−454.641156	−454.171437
Recombination Energy ^e					
RE(adenine-N-1-H) ⁺	−4.58		−4.53	−4.56	−4.54
RE(guanine-N-7-H) ⁺	−4.62		−4.50	−4.57	−4.52
RE(cytosine-N-3-H) ⁺	−5.28		−5.24	−5.28	−5.25
RE(thymine-O-4-H) ⁺	−5.57		−5.54	−5.56	−5.52

^aTotal energies in hartrees, 1 hartree = 2625.5 kJ mol^{−1}. ^bUnscaled zero point energies in kJ mol^{−1} from B3LYP/6-31+G(d,p) harmonic vibrational analysis. ^cSingle-point calculations on M06-2X/6-31+G(d,p) optimized geometries. ^dEffective single-point energies from basis set expansion to the complete basis set via spin-projected PMP2 energies: $E[\text{CCSD(T)/CBS}] \cong E[\text{ROHF/aug-cc-pVQZ}] + \Delta E_{\text{corr}}[\text{PMP2/CBS}] + E[\text{CCSD(T)/aug-cc-pVDZ}] - E[\text{PMP2/aug-cc-pVDZ}]$.

^eAdiabatic recombination energies at 0 K in electron volts.

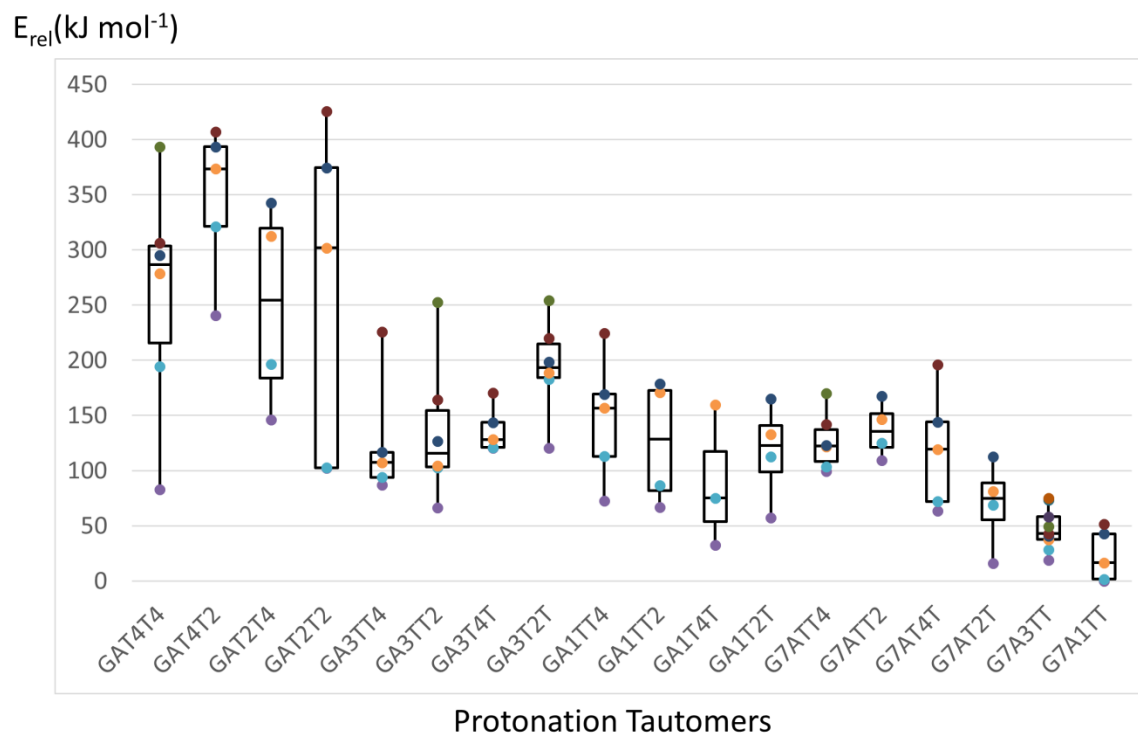


Fig. S1. Ranges of $\omega\text{B97X-D/6-31+G(d,p)}$ calculated relative free energies for conformers of 18 $(\text{GATT}+2\text{H})^{2+}$ tautomers. The ranges show maxima and minima, the boxes indicate first and third quartiles and medians.

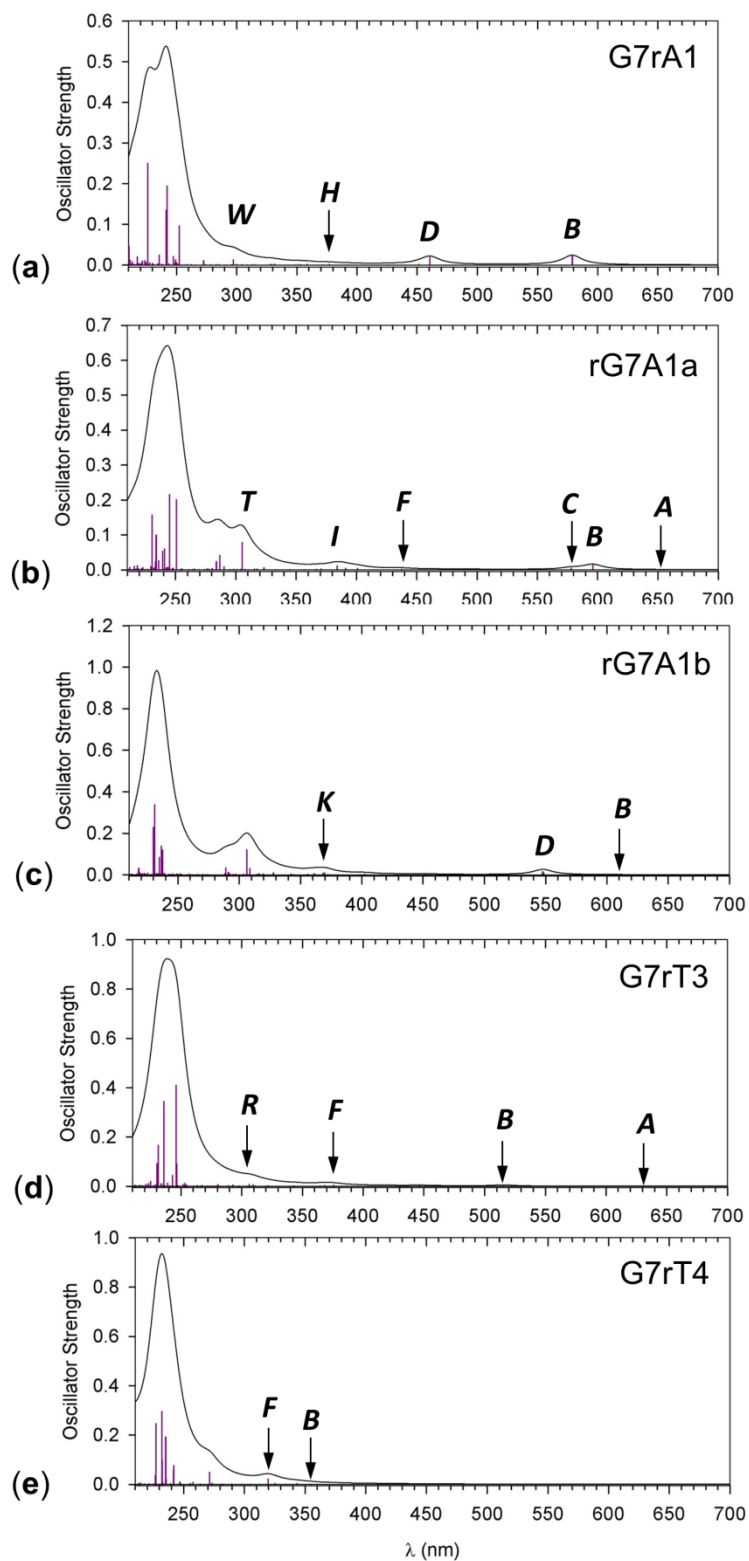


Fig. S2. M06-2X/6-31+G(d,p) TD-DFT absorption spectra of (a) adenine radical **G7rA1**, (b),(c) guanine radicals **rG7A1a** and **rG7A1b**, (d) thymine-3 radical **G7rT3**, (e) thymine-4 radical **G7rT4**. The bands are from artificial Lorentzian broadening of the excitation lines with at 10 nm full width at half maximum.

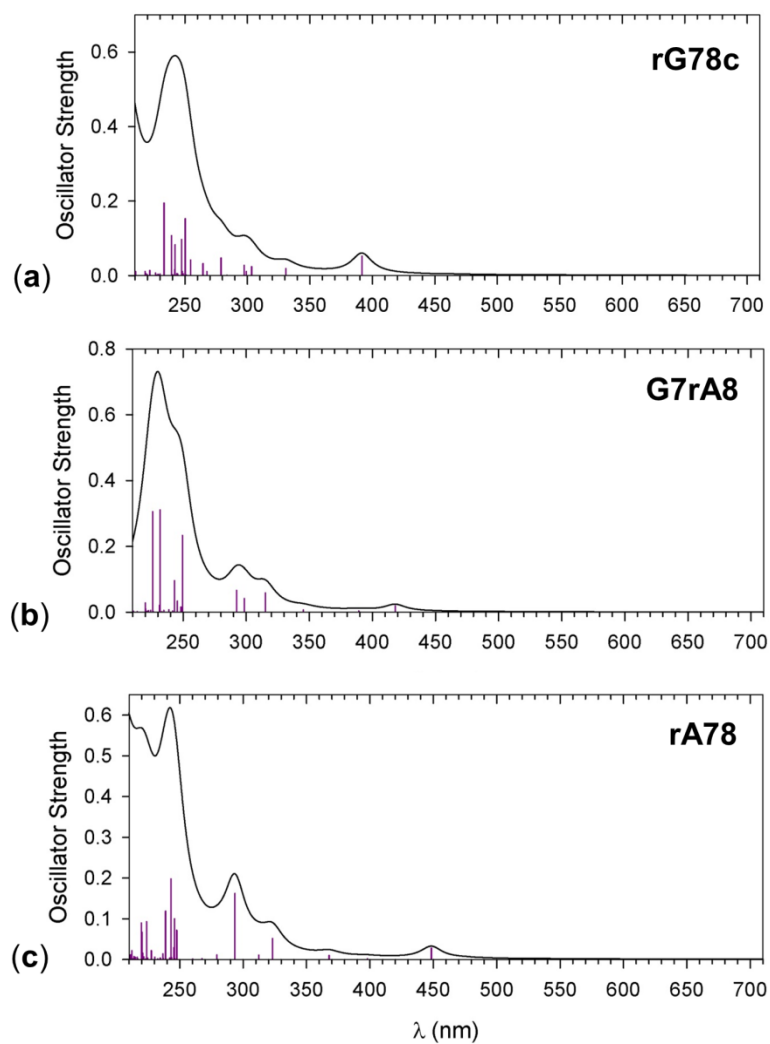


Fig. S3. M06-2X/6-31+G(d,p) TD-DFT absorption spectra of (a) adenine radical **G7rA8**, (b) guanine radical **rG78c**, (c) adenine radical **rA78**. The bands are from artificial Lorentzian broadening of the excitation lines at 10 nm full width at half maximum.

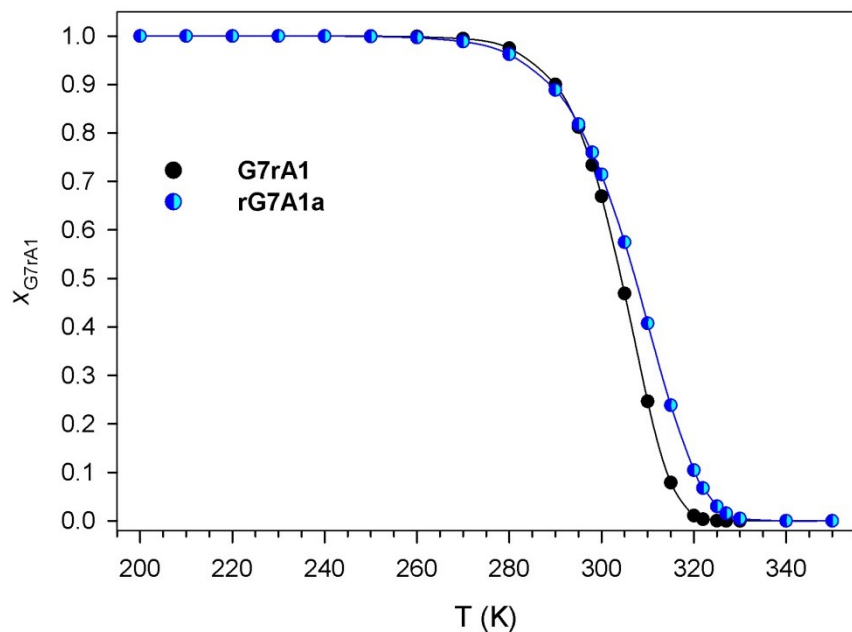


Fig. S4. Temperature-dependent mole fractions of **G7rA1** and **rG7A1a** isomerizing to **rG78b** via **TS1** within 150 ms.

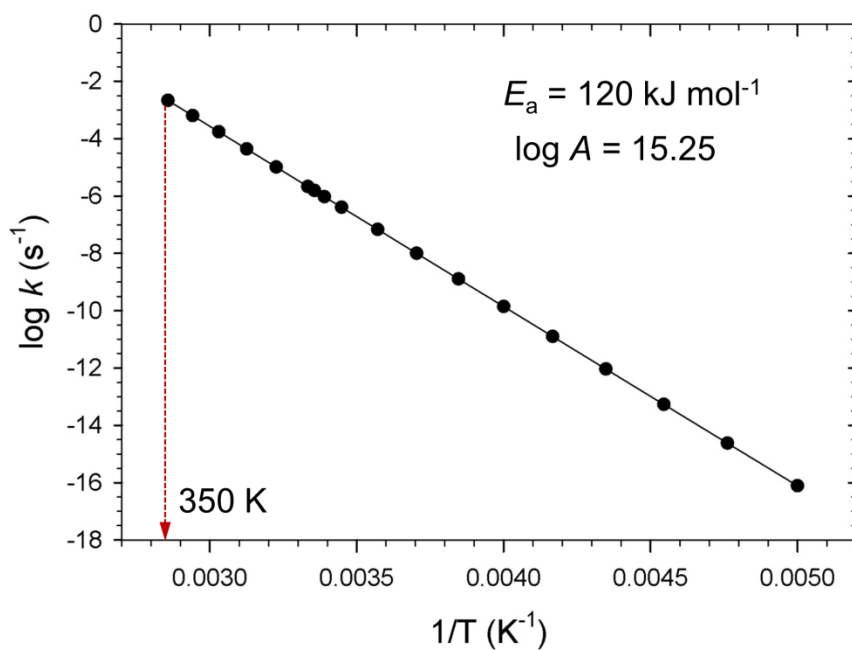
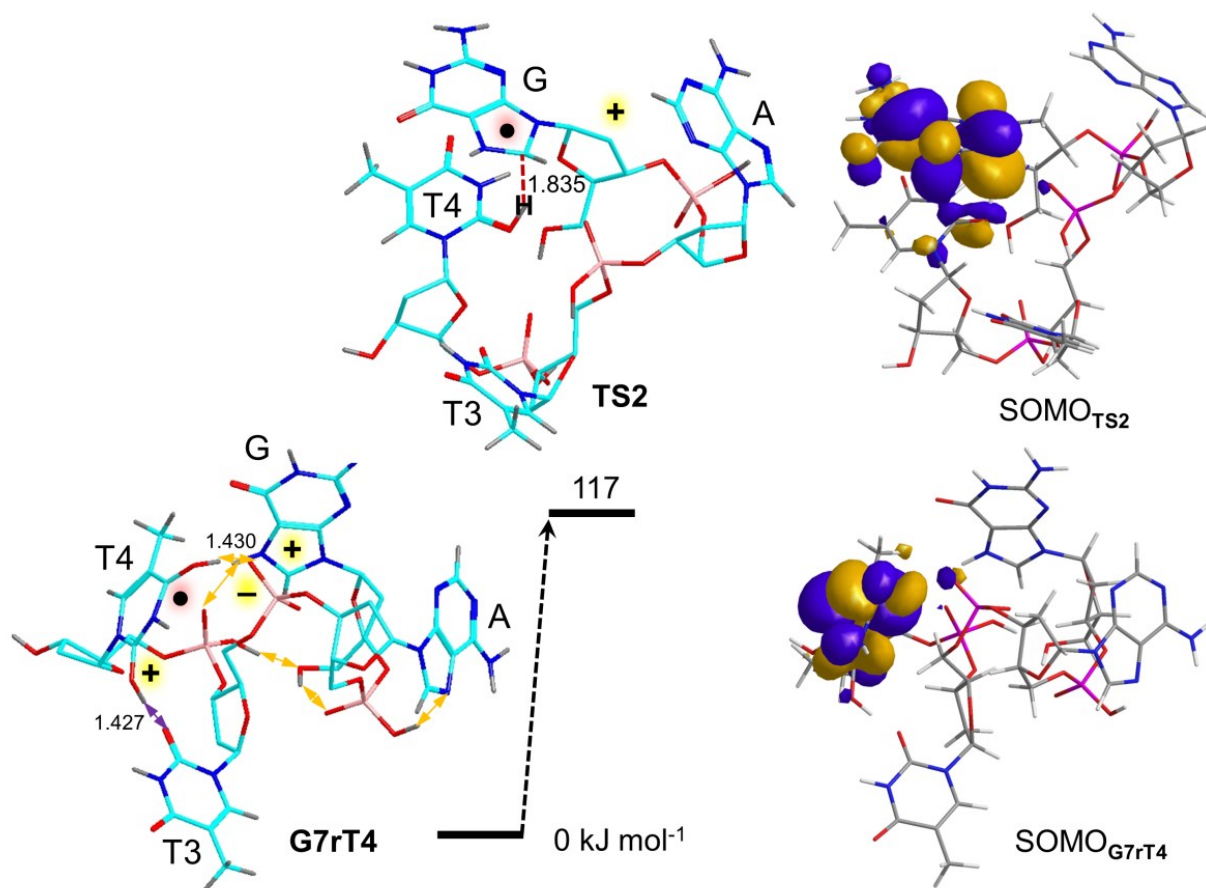


Fig. S5. Arrhenius plot of calculated TST rate constants for **G7rT4** isomerizing via **TS2**.



Scheme S1. Hydrogen atom migration in **G7rT4**. The right panel shows the singly-occupied molecular orbitals (SOMO) for the **G7rT4** reactant and **TS2**.