Correlated Triplet Pair Formation Activated by Geometry Relaxation in Directly Linked Tetracene Dimer (5,5'-Bitetracene)

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Full geometry optimization and frequency analysis of $^1(S_0S_0)$ of 55BT

The geometry of ground state, $^1(S_0S_0)$, of 55BT was optimized at the $ωB97X-D/6-31G(d)$ level of theory assuming that 55BT belonged to the $C_2$ point group and then, its stability was confirmed using frequency analysis at the same level of theory. No imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package. The standard nuclear orientation and tube representation of the stable geometry are shown in Table S1 and Figure S1, respectively.

Full geometry optimization and frequency analysis of $^1(S_0S_1)$ of 55BT

First, the geometry of $^1(S_0S_1)$ of 55BT was optimized at the TD-$ωB97X-D/6-31G(d)$ level of theory assuming that 55BT belonged to the $C_2$ point group and then, its stability was examined using frequency analysis at the same level of theory. From the frequency analysis, the optimized geometry had a single imaginary mode which broke the $C_2$ symmetry. Second, the geometry was optimized again at the TD-$ωB97X-D/6-31G(d)$ level of theory assuming that 55BT belonged to the $C_1$ point group and then, its stability was examined using frequency analysis at the same level of theory. This time, no imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package. The standard nuclear orientation and tube representation of the stable geometry are shown in Table S2 and Figure S1, respectively.

Full geometry optimization and frequency analysis of $^5(T_1T_1)$ of 55BT

The geometry of $^5(T_1T_1)$ of 55BT was optimized at the U$ωB97X-D/6-31G(d)$ level of theory assuming that 55BT belonged to the $C_2$ point group and then, its stability was confirmed using frequency analysis at the same level of theory. No imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package. The standard nuclear orientation and tube representation of the stable geometry are shown in Table S3 and Figure S1, respectively.
Full geometry optimization and frequency analysis of S₀ of Tetracene (Tc)

The geometry of ground state, S₀, of Tc was optimized at the ωB97X-D/6-31G(d) level of theory assuming that Tc belonged to the D₄h point group and then, its stability was confirmed using frequency analysis at the same level of theory. No imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package.¹ The standard nuclear orientation and tube representation of the stable geometry are shown in Table S4 and Figure S1, respectively.

Full geometry optimization and frequency analysis of S₁ of Tc

The geometry of S₁ of Tc was optimized at the TD-ωB97X-D/6-31G(d) level of theory assuming that Tc belonged to the D₂h point group and then, its stability was confirmed using frequency analysis at the same level of theory. No imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package.¹ The standard nuclear orientation and tube representation of the stable geometry are shown in Table S5 and Figure S1, respectively.

Full geometry optimization and frequency analysis of T₁ of Tc

The geometry of T₁ of Tc was optimized at the UωB97X-D/6-31G(d) level of theory assuming that Tc belonged to the D₂h point group and then, its stability was confirmed using frequency analysis at the same level of theory. No imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package.¹ The standard nuclear orientation and tube representation of the stable geometry are shown in Table S6 and Figure S1, respectively.
Table S1. Standard nuclear orientation of $^1$($S_0$,$S_0$) geometry of 55BT optimized at the ωB97X-D/6-31G(d) level of theory assuming that 55BT belongs to the $C_2$ point group.

| Atom | Element symbol | x (Å) | y (Å) | z (Å) |
|------|----------------|-------|-------|-------|
| 1    | C              | -0.214199 | 0.715293 | -0.893850 |
| 2    | C              | -1.234748 | 1.143955 | -1.744652 |
| 3    | C              | -1.646628 | 2.526533 | -1.732445 |
| 4    | C              | -1.025843 | 3.418320 | -0.874483 |
| 5    | C              | 0.003102  | 3.010173 | -0.007077 |
| 6    | C              | 0.420082  | 1.631555 | -0.013936 |
| 7    | C              | 1.450971  | 1.236582 | 0.862118  |
| 8    | C              | 2.064613  | 2.135771 | 1.720135  |
| 9    | C              | 1.646628  | 3.515153 | 1.724898  |
| 10   | C              | 2.297795  | 4.427149 | 2.622376  |
| 11   | C              | 3.287484  | 4.002326 | 3.451523  |
| 12   | C              | 3.113998  | 1.734372 | 2.613675  |
| 13   | C              | -1.904619 | 0.247093 | -2.646681 |
| 14   | C              | -2.896608 | 0.686983 | -3.465254 |
| 15   | C              | -3.02371  | 2.058726 | -3.452338 |
| 16   | H              | -1.339006 | 4.460159 | -0.867308 |
| 17   | H              | 1.773070  | 0.199491 | 0.864750  |
| 18   | H              | 0.314084  | 4.955101 | 0.866312  |
| 19   | H              | 1.980268  | 5.466717 | 2.623458  |
| 20   | H              | 3.772478  | 4.701454 | 4.126214  |
| 21   | H              | 4.495567  | 2.316081 | 4.119020  |
| 22   | H              | 3.425903  | 0.693323 | 2.607556  |
| 23   | H              | -1.601766 | -0.794607 | -2.662399 |
| 24   | H              | -3.390575 | -0.006515 | -4.139108 |
| 25   | H              | -4.097004 | 2.386166 | -4.115984 |
| 26   | C              | -3.000160 | 3.987290 | -2.599753 |
| 27   | C              | 0.214199  | -0.715293 | -0.893850 |
| 28   | C              | 1.234748  | -1.143955 | -1.744652 |
| 29   | C              | 1.646628  | -2.526533 | -1.732445 |
| 30   | C              | 1.025843  | -3.418320 | -0.874483 |
| 31   | C              | -0.003102 | -3.010173 | -0.007077 |
| 32   | C              | -0.420082 | -1.631555 | -0.013936 |
| 33   | C              | -1.450971 | -1.236582 | 0.862118  |
| 34   | C              | -2.064613 | -2.135771 | 1.720135  |
| 35   | C              | -1.646628 | -3.515153 | 1.724898  |
| 36   | C              | -0.634535 | -3.915392 | 0.867911  |
| 37   | C              | -2.297795 | -4.427149 | 2.622376  |
| 38   | C              | -3.287484 | -4.002326 | 3.451523  |
|   |   |   |   |
|---|---|---|---|
| 42 C | -3.702955 | -2.631998 | 3.447438 |
| 43 C | -3.113998 | -1.734372 | 2.613865 |
| 44 C | 1.904619  | -0.247093 | -2.646681 |
| 45 C | 2.896608  | -0.686983 | -3.465254 |
| 46 C | 3.302371  | -2.058726 | -3.452338 |
| 47 C | 2.698500  | -2.943142 | -2.616675 |
| 48 H | 1.339006  | -4.460159 | -0.867308 |
| 49 H | -1.773070 | -0.199491 | 0.864750  |
| 50 H | -0.314084 | -4.955101 | 0.866312  |
| 51 H | -1.980268 | -5.466717 | 2.623458  |
| 52 H | -3.772478 | -4.701454 | 4.126214  |
| 53 H | -4.495567 | -2.316081 | 4.119020  |
| 54 H | -3.425903 | -0.693323 | 2.607556  |
| 55 H | 1.601766  | 0.794607  | -2.662399 |
| 56 H | 3.390575  | 0.006515  | -4.139108 |
| 57 H | 4.097004  | -2.386166 | -4.115984 |
| 58 H | 3.000160  | -3.987290 | -2.599753 |
Table S2. Standard nuclear orientation of \(^1\text{(S}_0\text{S}_1)\) geometry of 55BT optimized at the TD-\(\omega\)B97X-D/6-31G(d) level of theory assuming that 55BT belongs to the \(C_1\) point group.

| Atom | Element symbol | x (Å)  | y (Å)  | z (Å)  |
|------|----------------|--------|--------|--------|
| 1    | C              | -0.486390 | -0.817017 | 0.565552 |
| 2    | C              | -0.266094 | -1.629058 | 1.682189 |
| 3    | C              | -1.216798 | -1.633184 | 2.766720 |
| 4    | C              | -2.346556 | -0.835285 | 2.690569 |
| 5    | C              | -2.591661 | -0.010134 | 1.578751 |
| 6    | C              | -1.642779 | 0.006356  | 0.495170 |
| 7    | C              | -1.890467 | 0.851714  | -0.603513 |
| 8    | C              | -3.023668 | 1.648763  | -0.671620 |
| 9    | C              | -3.977240 | 1.623684  | 0.408579 |
| 10   | C              | -3.738402 | 0.803604  | 1.499863 |
| 11   | C              | -5.142614 | 2.456210  | 0.315054 |
| 12   | C              | -5.345560 | 3.253054  | -0.767775 |
| 13   | C              | -4.398013 | 3.279153  | -1.840190 |
| 14   | C              | -3.279908 | 2.506645  | -1.792745 |
| 15   | C              | 0.884152  | -2.483018 | 1.788323 |
| 16   | C              | 1.079599  | -3.264440 | 2.883987 |
| 17   | C              | 0.140281  | -3.260644 | 3.961985 |
| 18   | C              | -0.966989 | -2.475075 | 3.902254 |
| 19   | H              | -3.063675 | -0.844109 | 3.508647 |
| 20   | H              | -1.172937 | 0.879867  | -1.418565 |
| 21   | H              | -4.451212 | 0.785190  | 2.321614 |
| 22   | H              | -5.860319 | 2.435048  | 1.131125 |
| 23   | H              | -6.231358 | 3.878424  | -0.827224 |
| 24   | H              | -4.581118 | 3.923712  | -2.694631 |
| 25   | H              | -2.557975 | 2.522902  | -2.604955 |
| 26   | H              | 1.597560  | -2.493290 | 0.970759 |
| 27   | H              | 1.956161  | -3.902379 | 2.945170 |
| 28   | H              | 0.317598  | -3.893174 | 4.826604 |
| 29   | H              | -1.688739 | -2.468899 | 4.715034 |
| 30   | C              | 0.483543  | -0.814052 | -0.563116 |
| 31   | C              | 0.219412  | -1.624305 | -1.712712 |
| 32   | C              | 1.155234  | -1.619341 | -2.800143 |
| 33   | C              | 2.317723  | -0.818853 | -2.701878 |
| 34   | C              | 2.589863  | -0.024183 | -1.585217 |
| 35   | C              | 1.643457  | -0.011159 | -0.483602 |
| 36   | C              | 1.914767  | 0.809005  | 0.614677 |
| 37   | C              | 3.084356  | 1.607081  | 0.704521 |
| 38   | C              | 4.023831  | 1.582700  | -0.377167 |
| 39   | C              | 3.742879  | 0.764387  | -1.496331 |
| 40   | C              | 5.184980  | 2.373372  | -0.287845 |
| 41   | C              | 5.423523  | 3.167022  | 0.826054 |
|   |   |   |   |   |
|---|---|---|---|---|
| 42 | C | 4.505259 | 3.191530 | 1.881457 |
| 43 | C | 3.350781 | 2.420713 | 1.818926 |
| 44 | C | -0.922508 | -2.438508 | -1.814790 |
| 45 | C | -1.155336 | -3.213757 | -2.946133 |
| 46 | C | -0.247303 | -3.202196 | -4.006833 |
| 47 | C | 0.894882 | -2.414918 | -3.930487 |
| 48 | H | 3.024842 | -0.823613 | -3.528831 |
| 49 | H | 1.206179 | 0.841127 | 1.437193 |
| 50 | H | 4.451414 | 0.749157 | -2.322047 |
| 51 | H | 5.898000 | 2.355824 | -1.108176 |
| 52 | H | 6.324811 | 3.770188 | 0.876776 |
| 53 | H | 4.693500 | 3.813552 | 2.751027 |
| 54 | H | 2.637037 | 2.438844 | 2.638415 |
| 55 | H | -1.631646 | -2.458816 | -0.993771 |
| 56 | H | -2.047379 | -3.830081 | -2.999107 |
| 57 | H | -0.429727 | -3.808176 | -4.888946 |
| 58 | H | 1.607561 | -2.406498 | -4.751303 |
Table S3. Standard nuclear orientation of $^{5}(T_{1}T_{1})$ geometry of 55BT optimized at the UoB97XD/6-31G(d) level of theory assuming that 55BT belongs to the $C_{2}$ point group.

| Atom | Element symbol | x (Å)   | y (Å)   | z (Å)   |
|------|----------------|---------|---------|---------|
| 1    | C              | -0.378923 | 0.638394 | -0.862158 |
| 2    | C              | -1.498920 | 0.792782 | -1.771854 |
| 3    | C              | -2.218079 | 2.020665 | -1.786130 |
| 4    | C              | -1.817694 | 3.074881 | -0.899402 |
| 5    | C              | -0.743771 | 2.940935 | -0.017160 |
| 6    | C              | 0.002609  | 1.682436 | 0.005194  |
| 7    | C              | 1.074354  | 1.560568 | 0.889414  |
| 8    | C              | 1.469310  | 2.620253 | 1.774968  |
| 9    | C              | 0.743771  | 3.842965 | 1.752907  |
| 10   | C              | -0.358535 | 3.970279 | 0.843569  |
| 11   | C              | 1.125618  | 4.878780 | 2.614305  |
| 12   | C              | 2.199308  | 4.722088 | 3.483739  |
| 13   | C              | 2.910677  | 3.522684 | 3.505650  |
| 14   | C              | 2.546787  | 2.482348 | 2.657582  |
| 15   | C              | -1.896167 | -0.232440| -2.637558 |
| 16   | C              | -2.973840 | -0.062375| -3.502480 |
| 17   | C              | -3.676451 | 1.139288 | -3.512827 |
| 18   | C              | -3.298558 | 2.170777 | -2.662679 |
| 19   | H              | -2.373943 | 4.009093 | 0.916619  |
| 20   | H              | 1.636393  | 0.631679 | 0.916619  |
| 21   | H              | -0.912662 | 4.905983 | 0.826743  |
| 22   | H              | 0.570396  | 5.813281 | 2.596618  |
| 23   | H              | 2.482451  | 5.535180 | 4.145262  |
| 24   | H              | 3.749051  | 3.399160 | 4.184349  |
| 25   | H              | 3.099801  | 1.546721 | 2.673044  |
| 26   | H              | -1.353670 | -1.172633| -2.629972 |
| 27   | H              | -3.236329 | -0.872112| -4.165171 |
| 28   | H              | -4.517432 | 1.273895 | -4.189691 |
| 29   | H              | -3.844504 | 3.110881 | -2.668869 |
| 30   | C              | 0.378923  | -0.638394| -0.862158 |
| 31   | C              | 1.498920  | -0.792782| -1.771854 |
| 32   | C              | 2.218079  | -2.020665| -1.786130 |
| 33   | C              | 1.817694  | -3.074881| -0.899402 |
| 34   | C              | 0.743771  | -2.940935| -0.017160 |
| 35   | C              | -0.002609 | -1.682436| 0.005194  |
| 36   | C              | -1.074354 | -1.560568| 0.889414  |
| 37   | C              | -1.469310 | -2.620253| 1.774968  |
| 38   | C              | -0.743771 | -3.842965| 1.752907  |
| 39   | C              | 0.358535  | -3.970279| 0.843569  |
| 40   | C              | -1.125618 | -4.878780| 2.614305  |
| 41   | C              | -2.199308 | -4.722088| 3.483739  |
|   |  |      |      |      |
|---|---|------|------|------|
| 42 | C | -2.910677 | -3.522684 | 3.505650 |
| 43 | C | -2.546787 | -2.482348 | 2.657582 |
| 44 | C | 1.896167  | 0.232440  | -2.637558 |
| 45 | C | 2.973840  | 0.062375  | -3.502480 |
| 46 | C | 3.676451  | -1.139288 | -3.516287 |
| 47 | C | 3.298558  | -2.170777 | -2.662679 |
| 48 | H | 2.373943  | -4.009093 | -0.918654 |
| 49 | H | -1.636393 | -0.631679 | 0.916619  |
| 50 | H | 0.912662  | -4.905983 | 0.826743  |
| 51 | H | -0.570396 | -5.813281 | 2.596618  |
| 52 | H | -2.482451 | -5.535180 | 4.145262  |
| 53 | H | -3.749051 | -3.399160 | 4.184349  |
| 54 | H | -3.099801 | -1.546721 | 2.673044  |
| 55 | H | 1.353670  | 1.172633  | -2.629972 |
| 56 | H | 3.263294  | 0.872112  | -4.165171 |
| 57 | H | 4.517432  | -1.273895 | -4.189691 |
| 58 | H | 3.844504  | -3.110881 | -2.668869 |
Table S4. Standard nuclear orientation of S₀ geometry of Tc optimized at the ωB97X-D/6-31G(d) level of theory assuming that Tc belongs to the $D_{2h}$ point group.

| Atom | Element symbol | x (Å)   | y (Å)   | z (Å)   |
|------|----------------|---------|---------|---------|
| 1    | C              | 0.000000| 4.873620| 0.715886|
| 2    | C              | 0.000000| 3.702971| 1.406511|
| 3    | C              | 0.000000| 2.440783| 0.721150|
| 4    | C              | 0.000000| 2.440783|-0.721150|
| 5    | C              | 0.000000| 3.702971|-1.406511|
| 6    | C              | 0.000000| 4.873620|-0.715886|
| 7    | C              | 0.000000| 1.232962| 1.401392|
| 8    | C              | 0.000000| 1.232962|-1.401392|
| 9    | C              | 0.000000| 0.000000|-0.719988|
| 10   | C              | 0.000000| 0.000000| 0.719988 |
| 11   | C              | 0.000000|-1.232962| 1.401392 |
| 12   | H              | 0.000000|-1.231802| 2.488863 |
| 13   | C              | 0.000000|-2.440783| 0.721150 |
| 14   | C              | 0.000000|-2.440783|-0.721150|
| 15   | C              | 0.000000|-1.232962|-1.401392|
| 16   | H              | 0.000000| 1.231802| 2.488863|
| 17   | H              | 0.000000| 5.821156| 1.245787|
| 18   | H              | 0.000000| 3.699915| 2.493051|
| 19   | H              | 0.000000| 3.699915|-2.493051|
| 20   | H              | 0.000000| 5.821156|-1.245787|
| 21   | H              | 0.000000| 1.231802|-2.488863|
| 22   | H              | 0.000000|-1.231802|-2.488863|
| 23   | C              | 0.000000|-3.702971|-1.406511|
| 24   | C              | 0.000000|-3.702971| 1.406511 |
| 25   | C              | 0.000000|-4.873620|-0.715886|
| 26   | C              | 0.000000|-4.873620| 0.715886 |
| 27   | H              | 0.000000|-3.699915|-2.493051|
| 28   | H              | 0.000000|-5.821156|-1.245787|
| 29   | H              | 0.000000|-5.821156| 1.245787 |
| 30   | H              | 0.000000|-3.699915| 2.493051 |
Table S5. Standard nuclear orientation of $S_1$ geometry of Tc optimized at the TD-ωB97X-D/6-31G(d) level of theory assuming that Tc belongs to the $D_{2h}$ point group.

| Atom | Element symbol | x (Å)    | y (Å)    | z (Å)    |
|------|----------------|----------|----------|----------|
| 1    | C              | 0.000000 | 4.905403 | 0.698672 |
| 2    | C              | 0.000000 | 3.702090 | 1.396151 |
| 3    | C              | 0.000000 | 2.471115 | 0.717485 |
| 4    | C              | 0.000000 | 2.471115 | -0.717485|
| 5    | C              | 0.000000 | 3.702090 | -1.396151|
| 6    | C              | 0.000000 | 4.905403 | -0.698672|
| 7    | C              | 0.000000 | 1.227293 | 1.397932 |
| 8    | C              | 0.000000 | 1.227293 | -1.397932|
| 9    | C              | 0.000000 | 0.000000 | -0.726338|
| 10   | C              | 0.000000 | 0.000000 | 0.726338 |
| 11   | C              | 0.000000 | -1.227293| 1.397932 |
| 12   | H              | 0.000000 | -1.230717| 2.485889 |
| 13   | C              | 0.000000 | -2.471115| 0.717485 |
| 14   | C              | 0.000000 | -2.471115| -0.717485|
| 15   | C              | 0.000000 | -1.227293| -1.397932|
| 16   | H              | 0.000000 | 1.230717 | 2.485889 |
| 17   | H              | 0.000000 | 5.845280 | 1.241811 |
| 18   | H              | 0.000000 | 3.702332 | 2.483089 |
| 19   | H              | 0.000000 | 3.702332 | -2.483089|
| 20   | H              | 0.000000 | 5.845280 | -1.241811|
| 21   | H              | 0.000000 | 1.230717 | -2.485889|
| 22   | H              | 0.000000 | -1.230717| -2.485889|
| 23   | C              | 0.000000 | -3.702090| -1.396151|
| 24   | C              | 0.000000 | -3.702090| 1.396151 |
| 25   | C              | 0.000000 | -4.905403| -0.698672|
| 26   | C              | 0.000000 | -4.905403| 0.698672 |
| 27   | H              | 0.000000 | -3.702332| -2.483089|
| 28   | H              | 0.000000 | -5.845280| -1.241811|
| 29   | H              | 0.000000 | -5.845280| 1.241811 |
| 30   | H              | 0.000000 | -3.702332| 2.483089 |
Table S6. Standard nuclear orientation of T₁ geometry of Tc optimized at the UωB97X-D/6-31G(d) level of theory assuming that Tc belongs to the $D_{2h}$ point group.

| Atom | Element symbol | x (Å)   | y (Å)   | z (Å)   |
|------|----------------|---------|---------|---------|
| 1    | C              | 0.000000| 4.911163| 0.696757|
| 2    | C              | 0.000000| 3.705999| 1.392618|
| 3    | C              | 0.000000| 2.483646| 0.711641|
| 4    | C              | 0.000000| 2.483646|-0.711641|
| 5    | C              | 0.000000| 3.705999|-1.392618|
| 6    | C              | 0.000000| 4.911163|-0.696757|
| 7    | C              | 0.000000| 1.224441| 1.403957|
| 8    | C              | 0.000000| 1.224441|-1.403957|
| 9    | C              | 0.000000| 0.000000|-0.732116|
| 10   | C              | 0.000000| 0.000000| 0.732116|
| 11   | C              | 0.000000|-1.224441| 1.403957|
| 12   | H              | 0.000000|-1.231296| 2.491463|
| 13   | C              | 0.000000|-2.483646| 0.711641|
| 14   | C              | 0.000000|-2.483646|-0.711641|
| 15   | C              | 0.000000|-1.224441|-1.403957|
| 16   | H              | 0.000000| 1.231296| 2.491463|
| 17   | H              | 0.000000| 5.850207| 1.241757|
| 18   | H              | 0.000000| 3.705286| 2.479735|
| 19   | H              | 0.000000| 3.705286|-2.479735|
| 20   | H              | 0.000000| 5.850207|-1.241757|
| 21   | H              | 0.000000| 1.231296|-2.491463|
| 22   | H              | 0.000000|-1.231296|-2.491463|
| 23   | C              | 0.000000|-3.705999|-1.392618|
| 24   | C              | 0.000000|-3.705999| 1.392618|
| 25   | C              | 0.000000|-4.911163|-0.696757|
| 26   | C              | 0.000000|-4.911163| 0.696757|
| 27   | H              | 0.000000|-3.705286|-2.479735|
| 28   | H              | 0.000000|-5.850207|-1.241757|
| 29   | H              | 0.000000|-5.850207| 1.241757|
| 30   | H              | 0.000000|-3.705286| 2.479735|
Figure S1. Stable \(^1(S_0S_0)\), \(^1(S_0S_1)\), and \(^5(T_1T_1)\) geometries of 55BT and stable \(S_0\), \(S_1\), and \(T_1\) geometries of tetracene. For \(^1(S_0S_0)\) of 55BT and \(S_0\) of tetracene, geometry optimization was done using the \(\omega B97X-D/6-31G(d)\) method; for \(^1(S_0S_1)\) of 55BT and \(S_1\) of tetracene, geometry optimization was done using the TD-\(\omega B97X-D/6-31G(d)\) method; for \(^5(T_1T_1)\) of 55BT and \(T_1\) of tetracene, geometry optimization was done using the U\(\omega B97X-D/6-31G(d)\) method. All the H atoms are omitted for clarity. Numbers show representative C–C bond lengths (Å) and the torsion angle between the two tetracene units (degree).
Method of calculating electronic states of 55BT

The wave functions of \( ^1(S_0S_0) \), \( ^1(S_0S_1) \), \( ^1(S_0S_1)' \), \( ^5(T_1T_1) \), and \( ^5(T_1T_1) \) for the stable \(^1(S_0S_0)\), \(^1(S_0S_1)\), and \(^5(T_1T_1)\) geometries were calculated using a configuration interaction (CI) method called the RAS-2SF approach with four electrons in four orbitals (denoted as RAS(4,4)-2SF/6-31G(d)). The reference electronic configuration for the RAS(4,4)-2SF/6-31G(d) calculation was obtained using the ROHF/6-31G(d) method. The active space was divided into three subspaces, RAS1, RAS2, and RAS3. RAS2 consisted of HOMO−1, HOMO, LUMO, and LUMO+1. RAS1 consisted of occupied orbitals with energies lower than that of the HOMO−1 (HOMO−2, HOMO−3, ⋯) and RAS3 consisted of unoccupied orbitals with energies higher than that of the LUMO+1 (LUMO+2, LUMO+3, ⋯). The RAS-2SF calculations were performed using the Q-Chem program package. The RAS-CI code written by David Casanova was used for the RAS-2SF calculations. Slater determinants dominantly contributing to \(^1(S_0S_0)\), \(^1(S_0S_1)\), \(^1(S_0S_1)'\), and \(^5(T_1T_1)\) for the optimized \(^1(S_0S_0)\), \(^1(S_0S_1)\), and \(^5(T_1T_1)\) geometries are listed in Table S7, S8, and S9, respectively.

Method of calculating energy differences between electronic states of 55BT

The electronic energies of \(^1(S_0S_1)\), \(^1(S_0S_1)'\), \(^5(T_1T_1)\), and \(^5(T_1T_1)\) as calculated using the RAS(4,4)-2SF/6-31G(d) method are denoted as \( E^{\text{RAS}}[^1(S_0S_1)] \), \( E^{\text{RAS}}[^1(S_0S_1)'] \), \( E^{\text{RAS}}[^5(T_1T_1)] \), and \( E^{\text{RAS}}[^5(T_1T_1)] \), respectively. Corrected electronic energies of \(^1(S_0S_1)\), \(^1(S_0S_1)'\), \(^5(T_1T_1)\), and \(^5(T_1T_1)\) are denoted as \( E^{\text{Corr}}[^1(S_0S_1)] \), \( E^{\text{Corr}}[^1(S_0S_1)'] \), \( E^{\text{Corr}}[^5(T_1T_1)] \), and \( E^{\text{Corr}}[^5(T_1T_1)] \), respectively. The energy corrections of \(^1(S_0S_1)\), \(^1(S_0S_1)'\), \(^5(T_1T_1)\), and \(^5(T_1T_1)\) are denoted as \( E^{\text{Corr}}[^1(S_0S_1)] \), \( E^{\text{Corr}}[^1(S_0S_1)'] \), \( E^{\text{Corr}}[^5(T_1T_1)] \), and \( E^{\text{Corr}}[^5(T_1T_1)] \) account for the dynamic correlation that the RAS(4,4)-2SF/6-31G(d) method was unable to take into account. The method of calculating \( E^{\text{Corr}}[^1(S_0S_1)] \), \( E^{\text{Corr}}[^1(S_0S_1)'] \), \( E^{\text{Corr}}[^5(T_1T_1)] \), and \( E^{\text{Corr}}[^5(T_1T_1)] \) has been described elsewhere. The calculated \( E^{\text{RAS}}[^1(S_0S_1)] \), \( E^{\text{RAS}}[^1(S_0S_1)'] \), \( E^{\text{RAS}}[^5(T_1T_1)] \), and \( E^{\text{RAS}}[^5(T_1T_1)] \) are listed in Table S10. The calculated \( E^{\text{Corr}}[^1(S_0S_1)] \), \( E^{\text{Corr}}[^1(S_0S_1)'] \), \( E^{\text{Corr}}[^5(T_1T_1)] \), and \( E^{\text{Corr}}[^5(T_1T_1)] \) are listed in Table S11. The calculated \( E[^1(S_0S_1)] \), \( E[^1(S_0S_1)'] \), \( E[^5(T_1T_1)] \), and \( E[^5(T_1T_1)] \) are listed in Table S12.
Table S7. Slater determinants dominantly contributing to \(^1(S_0S_0), ^1(S_0S_1), ^1(S_0S_1)’, \text{ and } ^1(T_1T_1)\) of 55BT at the stable \(^1(S_0S_0)\) geometry calculated using the RAS(4,4)-2SF/6-31G(d) method. Calculated \(^1(S_0S_0) \rightarrow ^1(S_0S_1), ^1(S_0S_1) \rightarrow ^1(S_0S_1)’\), and \(^1(S_0S_0) \rightarrow ^1(T_1T_1)\) excitation energies \((E_{ex})\) and transition dipole moments \((\mu)\). \(E_{ex}\) and \(\mu\) are in eV and debye, respectively.

| State \(S\) | Slater determinant \(\Phi_0\) | Contribution | \(E_{ex}\) | \(\mu\) |
|-------------|-------------------------------|--------------|----------|-------|
| \(^1(S_0S_0)\) | \(\Phi^{LUMO}_{HOMO}^{HOMO}\) | 84.9284155 | 1.3073461 |       |
|              | \(\Phi^{LUMO+1}_{HOMO-1}^{HOMO-1}\) | 1.2986205 |          |       |
|              | \(\Phi^{LUMO+1}_{HOMO-1}^{HOMO}\) | 1.2801167 | 0.9837446 |       |
|              | \(\Phi^{LUMO+1}_{HOMO-1}^{HOMO}\) | 0.9714920 | 0.9710332 |       |
| \(^1(S_0S_1)\) | \(\Phi^{LUMO+1}_{HOMO}\) | 20.5506484 | 18.3819733 |       |
|              | \(\Phi^{LUMO+1}_{HOMO-1}\) | 20.5506484 | 18.3819733 |       |
| \(^1(S_0S_1)’\) | \(\Phi^{LUMO}_{HOMO-1}\) | 22.0466038 | 19.8422582 |       |
|              | \(\Phi^{LUMO+1}_{HOMO-1}\) | 22.0466038 | 19.8422582 |       |
| \(^1(T_1T_1)\) | \(\Phi^{LUMO}_{HOMO}^{HOMO}\) | 18.9278410 | 18.7177403 | 18.7003944 |
|              | \(\Phi^{LUMO+1}_{HOMO-1}^{HOMO-1}\) | 18.6324788 | 8.3403100 | 8.3403100 |
|              | \(\Phi^{LUMO+1}_{HOMO-1}^{HOMO}\) | 8.3403100 | 2.1122257 |       |
| Transition                  | Energy (eV) |
|----------------------------|-------------|
| LUMO-1 HOMO → LUMO+1 LUMO  | 2.112257    |
| LUMO+1 HOMO-1 HOMO         | 2.0581020   |
| LUMO+1 LUMO-1 HOMO         | 2.0581020   |
| LUMO+1 LUMO HOMO-1 HOMO    | 2.0581020   |
Table S8. Slater determinants dominantly contributing to \( ^1(S_0S_0) \), \( ^1(S_0S_1) \), \( ^1(S_0S_1)' \), and \( ^1(T_1T_1) \) of 55BT calculated at the stable \( ^1(S_0S_1) \) geometry using the RAS(4,4)-2SF/6-31G(d) method. Calculated \( ^1(S_0S_0) \rightarrow ^1(S_0S_1) \), \( ^1(S_0S_0) \rightarrow ^1(S_0S_1)' \), and \( ^1(S_0S_0) \rightarrow ^1(T_1T_1) \) excitation energies \( (E_{ex}) \) and transition dipole moments \( (\mu) \). \( E_{ex} \) and \( \mu \) are in eV and debye, respectively.

| State    | Slater determinant | CI coefficient | \( E_{ex} \) | \( \mu \) |
|----------|--------------------|----------------|-------------|---------|
| \( ^1(S_0S_0) \) | \( \Phi_0 \) | 82.5169076 |             |         |
|          | \( \Phi_{LUMO}^{HOMO} \) | 6.7902840 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO-1} \) | 3.7745069 |             |         |
| \( ^1(S_0S_1) \) | \( \Phi_{LUMO}^{HOMO} \) | 34.8593506 | 3.7671      | 2.6503  |
|          | \( \Phi_{LUMO}^{HOMO} \) | 34.8593506 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO-1} \) | 3.3717643 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO-1} \) | 3.3717643 |             |         |
| \( ^1(S_0S_1)' \) | \( \Phi_{LUMO}^{HOMO-1} \) | 37.3048079 | 3.9860      | 0.6962  |
|          | \( \Phi_{LUMO}^{HOMO-1} \) | 37.3048079 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO-1} \) | 2.2892716 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO-1} \) | 2.2892716 |             |         |
| \( ^1(T_1T_1) \) | \( \Phi_{LUMO}^{HOMO-1} \) | 26.3859334 | 3.1082      | 0.0075  |
|          | \( \Phi_{LUMO+1}^{HOMO} \) | 26.3859334 |             |         |
|          | \( \Phi_{LUMO}^{HOMO-1} \) | 7.9395642 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO-1} \) | 7.9395642 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO} \) | 5.3777646 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO} \) | 5.3777646 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO} \) | 4.4652101 |             |         |
|          | \( \Phi_{LUMO+1}^{HOMO} \) | 4.4652101 |             |         |
|          | \( \Phi_{LUMO}^{HOMO-1} \) | 2.3699630 |             |         |
|          | \( \Phi_{LUMO}^{HOMO-1} \) | 2.3699630 |             |         |
|          | \( \Phi_{LUMO}^{HOMO-1} \) | 1.1039091 |             |         |
|          | \( \Phi_{LUMO}^{HOMO-1} \) | 1.1039091 |             |         |
Table S9. Slater determinants dominantly contributing to $^1(S_0S_0)$, $^1(S_0S_1)$, $^1(S_0S_1)'$, and $^1(T_1T_1)$ of 55BT calculated at the stable $^5(T_1T_1)$ geometry using the RAS(4,4)-2SF/6-31G(d) method. Calculated $^1(S_0S_0) \rightarrow ^1(S_0S_1)$, $^1(S_0S_0) \rightarrow ^1(S_0S_1)'$, and $^1(S_0S_0) \rightarrow ^1(T_1T_1)$ excitation energies ($E_{ex}$) and transition dipole moments ($\mu$). $E_{ex}$ and $\mu$ are in eV and debye, respectively.

| State       | Slater determinant   | CI coefficient | $E_{ex}$ | $\mu$  |
|-------------|----------------------|----------------|---------|--------|
| $^1(S_0S_0)$ | $^{\phi}_{LUMO\over HOMO}$ $^{\phi}_{LUMO\over HOMO}$ | 2.4363953     |         |        |
|             | $^{\phi}_{LUMO+1\over HOMO-1}$ $^{\phi}_{LUMO+1\over HOMO-1}$ | 2.4040161     |         |        |
|             | $^{\phi}_{LUMO+1\over HOMO-1}$ $^{\phi}_{LUMO\over HOMO}$ | 2.3585609     |         |        |
|             | $^{\phi}_{LUMO+1\over HOMO-1}$ $^{\phi}_{LUMO\over HOMO}$ | 2.3585609     |         |        |
|             | $^{\phi}_{LUMO\over HOMO-1}$ $^{\phi}_{LUMO+1\over HOMO}$ | 2.0128205     |         |        |
|             | $^{\phi}_{LUMO\over HOMO-1}$ $^{\phi}_{LUMO+1\over HOMO}$ | 2.0128205     |         |        |
|             | $^{\phi}_{LUMO\over HOMO-1}$ $^{\phi}_{LUMO\over HOMO}$ | 1.9765439     |         |        |
|             | $^{\phi}_{LUMO\over HOMO-1}$ $^{\phi}_{LUMO+1\over HOMO}$ | 1.9532249     |         |        |
| $^1(S_0S_1)$ | $^{\phi}_{LUMO_{HOMO}+1}$ | 22.2434742    | 4.1781  | 0.1790 |
|             | $^{\phi}_{LUMO_{HOMO}+1}$ | 22.2434742    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}+1}$ | 17.2174833    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}+1}$ | 17.2174833    |         |        |
| $^1(S_0S_1)'$ | $^{\phi}_{LUMO_{HOMO}+1}$ | 20.3313374    | 4.3380  | 0.0210 |
|             | $^{\phi}_{LUMO_{HOMO}+1}$ | 20.3313374    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}+1}$ | 19.1283410    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}+1}$ | 19.1283410    |         |        |
| $^1(T_1T_1)$ | $^{\phi}_{LUMO_{HOMO}-1}\over^{\phi}_{LUMO_{HOMO}}$ | 18.8992721    | 3.8316  | 0.0001 |
|             | $^{\phi}_{LUMO_{HOMO}-1}\over^{\phi}_{LUMO_{HOMO}}$ | 18.8928206    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}-1}\over^{\phi}_{LUMO_{HOMO}}$ | 18.6331567    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}}\over^{\phi}_{LUMO_{HOMO}}$ | 18.5536522    |         |        |
|             | $^{\phi}_{LUMO_{HOMO}}\over^{\phi}_{LUMO_{HOMO}}$ | 8.3403579     |         |        |
|             | $^{\phi}_{LUMO_{HOMO}-1}\over^{\phi}_{LUMO_{HOMO}}$ | 8.3403579     |         |        |
|             | $^{\phi}_{LUMO_{HOMO}}\over^{\phi}_{LUMO_{HOMO}}$ | 2.0779212     |         |        |
Table S10. The electronic energies of $^1(S_0S_0)$, $^1(S_0S_1)$, $^1(S_0S_1)'$, $^1(T_1T_1)$, and $^5(T_1T_1)$ at the stable $^1(S_0S_0)$, $^1(S_0S_1)$, and $^5(T_1T_1)$ geometries as calculated using the RAS(4,4)-2SF/6-31G(d) method. The zero point of the electronic energies is set to be the $^1(S_0S_0)$ energy calculated at the stable $^1(S_0S_0)$ geometry. Values are in eV.

|          | $^1(S_0S_0)$ | $^1(S_0S_1)$ | $^5(T_1T_1)$ |
|----------|-------------|-------------|-------------|
| $E^\text{RAS}[^1(S_0S_0)]$ | 0.0000 | 0.3067 | 0.8324 |
| $E^\text{RAS}[^1(S_0S_1)]$ | 4.1781 | 4.0738 | 4.3673 |
| $E^\text{RAS}[^1(S_0S_1)']$ | 4.3380 | 4.2927 | 4.3773 |
| $E^\text{RAS}[^1(T_1T_1)]$ | 3.8316 | 3.4149 | 2.9247 |
| $E^\text{RAS}[^5(T_1T_1)]$ | 3.8089 | 3.4220 | 2.9032 |

Table S11. The energy corrections for $^1(S_0S_0)$, $^1(S_0S_1)$, $^1(S_0S_1)'$, and $^1(T_1T_1)$ at the stable $^1(S_0S_0)$, $^1(S_0S_1)$, and $^5(T_1T_1)$ geometries. Values are in eV.

|          | $^1(S_0S_0)$ | $^1(S_0S_1)$ | $^5(T_1T_1)$ |
|----------|-------------|-------------|-------------|
| $E^\text{Corr}[^1(S_0S_0)]$ | 0.9006 | 0.9637 | 1.0284 |
| $E^\text{Corr}[^1(S_0S_1)]$ | 0.9006 | 0.9637 | 1.0284 |
| $E^\text{Corr}[^1(S_0S_1)']$ | 0.3836 | 0.2320 | 0.2266 |
| $E^\text{Corr}[^5(T_1T_1)]$ | 0.3836 | 0.2320 | 0.2266 |

Table S12. Corrected energies of $^1(S_0S_0)$, $^1(S_0S_1)$, $^1(S_0S_1)'$, $^1(T_1T_1)$, and $^5(T_1T_1)$ at the stable $^1(S_0S_0)$, $^1(S_0S_1)$, and $^5(T_1T_1)$ geometries. The zero point of the electronic energies is set to be the $^1(S_0S_0)$ energy calculated at the stable $^1(S_0S_0)$ geometry. Values are in eV. The corrected energies are shown in Figure S2.

|          | $^1(S_0S_0)$ | $^1(S_0S_1)$ | $^5(T_1T_1)$ |
|----------|-------------|-------------|-------------|
| $E[^1(S_0S_0)]$ | 0.0000 | 0.3067 | 0.8324 |
| $E[^1(S_0S_1)]$ | 3.2775 | 3.1101 | 3.3389 |
| $E[^1(S_0S_1)']$ | 3.4374 | 3.3290 | 3.3489 |
| $E[^1(T_1T_1)]$ | 3.4480 | 3.1829 | 2.6981 |
| $E[^5(T_1T_1)]$ | 3.4253 | 3.1900 | 2.6766 |
| $E[^5(T_1T_1)] - E[^1(S_0S_1)]$ | 0.1705 | 0.0728 | -0.6408 |
| $E[^1(T_1T_1)] - E[^1(S_0S_1)']$ | 0.0106 | -0.1461 | -0.6508 |
| $E[^5(T_1T_1)] - E[^1(T_1T_1)]$ | -0.0228 | 0.0071 | -0.0215 |
Figure S2. Energy-level diagrams for relevant electronic states for SF calculated at the stable $^1(S_0S_0)$, $^1(S_0S_1)$, and $^5(T_1T_1)$ geometries. The electronic energies of $^1(S_0S_0)$, $^1(S_0S_1)$, $^1(S_0S_1)'$, $^1(T_1T_1)$, and $^5(T_1T_1)$ are the corrected RAS(4,4)-2SF/6-31G(d) energies listed in Table S12. The zero point of the electronic energies is set to be the $^1(S_0S_0)$ energy calculated at the optimized $^1(S_0S_0)$ geometry.
Table S13. Interstate vibronic-coupling constant ($V_m$) of the $m$th vibrational mode between $^1$(T$_1$T$_1$) and $^1$(S$_0$S$_1$) for 55BT calculated at the stable $^1$(S$_0$S$_1$) geometry. Vibrational factor $P_m$ for the $m$th vibrational mode. Contribution from the $m$th mode to $r_{IC}$ ($r_{IC,m}$). $r_{IC} = \Sigma_m r_{IC,m} = 3.45 \times 10^{11}$ s$^{-1}$. $V_m$, $P_m$, and $r_{IC,m}$ versus wavenumber plots are shown in Figure 3 in the main text.

| $m$ | Wavenumber (cm$^{-1}$) | $V_m$ $(10^{-4}$ a.u.$)$ | $V_m^2$ $(10^{-8}$ a.u.$)$ | $P_m$ | $r_{IC,m}$ $(10^{10}$ s$^{-1}$) |
|-----|----------------------|--------------------------|--------------------------|-----|----------------------|
| 1   | 7.94                 | 0.03859                  | 0.14891                  | 0.00577 | 0.38053 |
| 2   | 33.80                | 0.00734                  | 0.00539                  | 0.00136 | 0.00324 |
| 3   | 37.55                | 0.11389                  | 1.29710                  | 0.00122 | 0.70138 |
| 4   | 47.42                | 0.01707                  | 0.02915                  | 0.00097 | 0.01249 |
| 5   | 49.63                | 0.00193                  | 0.00037                  | 0.00092 | 0.00015 |
| 6   | 80.34                | 0.09945                  | 0.98893                  | 0.00057 | 0.25051 |
| 7   | 86.25                | 0.22059                  | 4.86600                  | 0.00053 | 1.14860 |
| 8   | 108.16               | 0.53183                  | 28.28400                 | 0.00043 | 5.33360 |
| 9   | 121.40               | 0.36965                  | 13.66400                 | 0.00038 | 2.29860 |
| 10  | 129.33               | 0.66784                  | 44.60100                 | 0.00036 | 7.04850 |
| 11  | 159.56               | 0.05395                  | 0.29107                  | 0.00029 | 0.03742 |
| 12  | 166.94               | 0.14979                  | 2.24370                  | 0.00028 | 0.27594 |
| 13  | 178.60               | 0.08347                  | 0.69672                  | 0.00026 | 0.08022 |
| 14  | 220.92               | 0.51587                  | 26.61200                 | 0.00021 | 2.49250 |
| 15  | 236.43               | 0.34467                  | 11.88000                 | 0.00020 | 1.04210 |
| 16  | 242.86               | 0.58561                  | 34.29400                 | 0.00019 | 2.93170 |
| 17  | 275.84               | 0.06805                  | 0.46301                  | 0.00017 | 0.03502 |
| 18  | 284.53               | 0.00970                  | 0.00942                  | 0.00017 | 0.00069 |
| 19  | 314.08               | 0.01148                  | 0.01319                  | 0.00015 | 0.00088 |
| 20  | 320.96               | 0.22461                  | 5.04500                  | 0.00015 | 0.32979 |
| 21  | 321.23               | 0.10417                  | 1.08510                  | 0.00015 | 0.07088 |
| 22  | 331.19               | 0.10529                  | 1.10860                  | 0.00014 | 0.07029 |
| 23  | 347.94               | 0.18492                  | 3.41950                  | 0.00014 | 0.20658 |
| 24  | 358.45               | 0.62052                  | 38.50500                 | 0.00013 | 2.25850 |
| 25  | 386.46               | 0.16919                  | 2.86250                  | 0.00012 | 0.15557 |
| 26  | 416.70               | 0.13626                  | 1.85670                  | 0.00011 | 0.09313 |
| 27  | 438.97               | 0.04805                  | 0.23089                  | 0.00011 | 0.01092 |
| 28  | 458.48               | 0.07400                  | 0.54764                  | 0.00010 | 0.02458 |
| 29  | 472.44               | 0.16051                  | 2.57630                  | 0.00010 | 0.11131 |
| 30  | 476.67               | 0.38001                  | 14.44100                 | 0.00010 | 0.61662 |
| 31  | 480.87               | 0.00675                  | 0.00456                  | 0.00010 | 0.00019 |
| 32  | 484.08               | 0.09518                  | 0.90589                  | 0.00009 | 0.03789 |
| 33  | 505.65               | 0.08462                  | 0.71597                  | 0.00009 | 0.02815 |
| 34  | 508.61               | 0.02107                  | 0.04438                  | 0.00009 | 0.00173 |
| 35  | 522.04               | 0.00260                  | 0.00068                  | 0.00008 | 0.00003 |
| 36  | 533.34               | 0.09769                  | 0.95431                  | 0.00008 | 0.03451 |
| 37  | 542.17               | 0.07660                  | 0.58669                  | 0.00008 | 0.02064 |
| 38  | 555.20               | 0.07508                  | 0.56369                  | 0.00008 | 0.01901 |
|   |    |     |     |     |     |
|---|----|-----|-----|-----|-----|
| 39 | 565.34 | 0.05833 | 0.34029 | 0.00007 | 0.01110 |
| 40 | 569.19 | 0.19676 | 3.87140 | 0.00007 | 0.12466 |
| 41 | 607.79 | 0.64359 | 41.42100 | 0.00006 | 1.16570 |
| 42 | 622.76 | 0.33243 | 11.05100 | 0.00006 | 0.29452 |
| 43 | 631.23 | 0.08418 | 0.70868 | 0.00006 | 0.01110 |
| 44 | 635.89 | 0.18755 | 3.51750 | 0.00006 | 0.08931 |
| 45 | 639.35 | 0.21414 | 4.58560 | 0.00005 | 0.11494 |
| 46 | 650.58 | 0.51054 | 26.06500 | 0.00005 | 0.62648 |
| 47 | 662.27 | 0.22768 | 5.18380 | 0.00005 | 0.11925 |
| 48 | 681.28 | 0.43132 | 18.60400 | 0.00005 | 0.39849 |
| 49 | 689.94 | 0.19432 | 3.77600 | 0.00005 | 0.07831 |
| 50 | 737.73 | 0.04311 | 0.18586 | 0.00004 | 0.00324 |
| 51 | 739.70 | 0.01920 | 0.03687 | 0.00004 | 0.00064 |
| 52 | 742.57 | 0.05608 | 0.31451 | 0.00004 | 0.00539 |
| 53 | 756.23 | 0.02017 | 0.04069 | 0.00004 | 0.00067 |
| 54 | 759.25 | 0.00308 | 0.00095 | 0.00004 | 0.00002 |
| 55 | 760.44 | 0.07110 | 26.06500 | 0.00003 | 0.15815 |
| 56 | 770.35 | 0.00728 | 0.00531 | 0.00003 | 0.00008 |
| 57 | 774.43 | 0.07208 | 0.51957 | 0.00003 | 0.00799 |
| 58 | 778.27 | 0.04833 | 0.23353 | 0.00003 | 0.00355 |
| 59 | 782.81 | 0.12508 | 1.56450 | 0.00003 | 0.02342 |
| 60 | 790.08 | 0.09853 | 0.97089 | 0.00003 | 0.01420 |
| 61 | 795.05 | 0.20475 | 4.19230 | 0.00003 | 0.06036 |
| 62 | 800.41 | 0.33467 | 11.20000 | 0.00003 | 0.15861 |
| 63 | 816.53 | 0.16398 | 2.68900 | 0.00003 | 0.03627 |
| 64 | 821.13 | 0.04554 | 0.20740 | 0.00003 | 0.00276 |
| 65 | 855.89 | 0.02329 | 0.05422 | 0.00003 | 0.00066 |
| 66 | 862.59 | 0.01693 | 0.02866 | 0.00003 | 0.00034 |
| 67 | 869.53 | 0.01017 | 0.01034 | 0.00003 | 0.00012 |
| 68 | 873.66 | 0.01287 | 0.01657 | 0.00003 | 0.00019 |
| 69 | 881.26 | 0.57855 | 33.47200 | 0.00003 | 0.37933 |
| 70 | 890.70 | 0.03041 | 0.09245 | 0.00003 | 0.00102 |
| 71 | 891.10 | 0.01772 | 0.03140 | 0.00002 | 0.00035 |
| 72 | 904.40 | 0.00031 | 0.00001 | 0.00002 | 0.00000 |
| 73 | 915.08 | 0.10193 | 1.03900 | 0.00002 | 0.01088 |
| 74 | 921.32 | 0.03197 | 0.10218 | 0.00002 | 0.00106 |
| 75 | 925.91 | 0.07299 | 0.53271 | 0.00002 | 0.00545 |
| 76 | 932.70 | 0.01160 | 0.01344 | 0.00002 | 0.00014 |
| 77 | 934.30 | 0.00862 | 0.00743 | 0.00002 | 0.00007 |
| 78 | 949.50 | 0.00887 | 0.00786 | 0.00002 | 0.00008 |
| 79 | 953.16 | 0.00586 | 0.00344 | 0.00002 | 0.00003 |
| 80 | 962.33 | 0.04374 | 0.19134 | 0.00002 | 0.00182 |
| 81 | 968.50 | 0.00973 | 0.00946 | 0.00002 | 0.00009 |
| 82 | 988.51 | 0.00248 | 0.00061 | 0.00002 | 0.00001 |
| 83 | 988.65 | 0.00125 | 0.00016 | 0.00002 | 0.00000 |
|   |        |         |         |         |         |
|---|--------|---------|---------|---------|---------|
| 84 | 989.80 | 0.00633 | 0.00401 | 0.00002 | 0.00004 |
| 85 | 990.27 | 0.00130 | 0.00017 | 0.00002 | 0.00000 |
| 86 | 1013.67| 0.00155 | 0.00024 | 0.00002 | 0.00000 |
| 87 | 1014.02| 0.00296 | 0.00088 | 0.00002 | 0.00001 |
| 88 | 1038.40| 0.07772 | 0.60402 | 0.00002 | 0.00501 |
| 89 | 1042.13| 0.01862 | 0.03467 | 0.00002 | 0.00029 |
| 90 | 1075.52| 0.18271 | 3.33830 | 0.00002 | 0.02613 |
| 91 | 1078.04| 1.27190 | 161.7700 | 0.00002 | 1.26130 |
| 92 | 1085.52| 0.42099 | 17.7230  | 0.00002 | 0.13665 |
| 93 | 1153.30| 0.09005 | 0.81081  | 0.00002 | 0.00569 |
| 94 | 1153.93| 0.19340 | 3.74040  | 0.00002 | 0.02621 |
| 95 | 1162.08| 0.45904 | 21.0720  | 0.00002 | 0.14609 |
| 96 | 1170.48| 0.32128 | 10.3220  | 0.00002 | 0.07079 |
| 97 | 1185.56| 0.43543 | 18.9600  | 0.00002 | 0.12754 |
| 98 | 1195.44| 0.12488 | 1.55950  | 0.00001 | 0.01036 |
| 99 | 1201.24| 0.06434 | 0.41395  | 0.00001 | 0.00501 |
|100 | 1205.53| 0.11352 | 1.28870  | 0.00001 | 0.00846 |
|101 | 1212.96| 0.10940 | 1.19680  | 0.00001 | 0.00778 |
|102 | 1219.60| 0.00295 | 0.00087  | 0.00001 | 0.00001 |
|103 | 1243.48| 0.05166 | 0.26687  | 0.00001 | 0.00167 |
|104 | 1245.46| 0.09340 | 0.87239  | 0.00001 | 0.00545 |
|105 | 1263.13| 0.05719 | 0.32702  | 0.00001 | 0.00200 |
|106 | 1263.93| 0.44047 | 19.4010  | 0.00001 | 0.11874 |
|107 | 1269.62| 0.16213 | 2.62860  | 0.00001 | 0.01598 |
|108 | 1296.15| 0.19061 | 3.63320  | 0.00001 | 0.02143 |
|109 | 1313.13| 0.26687 | 7.1220  | 0.00001 | 0.04123 |
|110 | 1323.71| 0.37470 | 14.0400  | 0.00001 | 0.08034 |
|111 | 1330.10| 0.20988 | 4.4050  | 0.00001 | 0.02503 |
|112 | 1333.56| 0.13165 | 1.73320  | 0.00001 | 0.00981 |
|113 | 1337.11| 0.23839 | 5.6830  | 0.00001 | 0.03205 |
|114 | 1340.82| 0.31954 | 10.2110  | 0.00001 | 0.05736 |
|115 | 1351.54| 0.03703 | 0.13709  | 0.00001 | 0.00076 |
|116 | 1357.09| 0.01653 | 0.02733  | 0.00001 | 0.00015 |
|117 | 1379.27| 0.29505 | 8.70550  | 0.00001 | 0.04695 |
|118 | 1406.82| 0.05523 | 0.30499  | 0.00001 | 0.00160 |
|119 | 1408.73| 0.09208 | 0.84795  | 0.00001 | 0.00444 |
|120 | 1420.71| 0.33428 | 11.17400 | 0.00001 | 0.05775 |
|121 | 1434.08| 0.02249 | 0.05058  | 0.00001 | 0.00026 |
|122 | 1444.05| 0.01115 | 0.01243  | 0.00001 | 0.00006 |
|123 | 1454.87| 0.00874 | 0.00763  | 0.00001 | 0.00004 |
|124 | 1461.88| 0.03965 | 0.15717  | 0.00001 | 0.00078 |
|125 | 1470.17| 0.00896 | 0.00802  | 0.00001 | 0.00004 |
|126 | 1487.66| 0.01026 | 0.01053  | 0.00001 | 0.00005 |
|127 | 1491.65| 0.05551 | 0.30815  | 0.00001 | 0.00148 |
|128 | 1503.08| 0.23596 | 5.56770  | 0.00001 | 0.02653 |
|   |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|
| 129| 1505.19 | 0.12201 | 1.48860 | 0.00001 | 0.00708 |
| 130| 1511.04 | 0.34253 | 11.73300 | 0.00001 | 0.05548 |
| 131| 1532.51 | 0.09720 | 0.94476 | 0.00001 | 0.00438 |
| 132| 1543.53 | 0.00645 | 0.00416 | 0.00001 | 0.00002 |
| 133| 1567.28 | 0.02010 | 0.04040 | 0.00001 | 0.00018 |
| 134| 1580.36 | 0.01499 | 0.02247 | 0.00001 | 0.00010 |
| 135| 1589.91 | 0.02592 | 0.06720 | 0.00001 | 0.00030 |
| 136| 1591.61 | 0.03749 | 0.14054 | 0.00001 | 0.00062 |
| 137| 1626.08 | 0.04042 | 0.16335 | 0.00001 | 0.00069 |
| 138| 1627.41 | 0.09760 | 0.95263 | 0.00001 | 0.00404 |
| 139| 1639.14 | 0.05978 | 0.35739 | 0.00001 | 0.00026 |
| 140| 1649.99 | 0.17880 | 3.19690 | 0.00001 | 0.01330 |
| 141| 1666.27 | 0.07027 | 0.49382 | 0.00001 | 0.00202 |
| 142| 1678.27 | 0.06034 | 0.36403 | 0.00001 | 0.00148 |
| 143| 1695.52 | 0.07740 | 0.59903 | 0.00001 | 0.00239 |
| 144| 1723.78 | 0.09505 | 0.90351 | 0.00001 | 0.00352 |
| 145| 1735.24 | 0.10775 | 1.16100 | 0.00001 | 0.00448 |
| 146| 3196.46 | 0.10651 | 1.13440 | 0.00000 | 0.00167 |
| 147| 3197.92 | 0.21836 | 4.76810 | 0.00000 | 0.00700 |
| 148| 3198.71 | 0.23678 | 5.60650 | 0.00000 | 0.00822 |
| 149| 3200.29 | 0.60122 | 36.14700 | 0.00000 | 0.05297 |
| 150| 3204.51 | 0.06183 | 0.38232 | 0.00000 | 0.00056 |
| 151| 3205.04 | 0.23542 | 5.54230 | 0.00000 | 0.00810 |
| 152| 3205.33 | 0.03675 | 0.13506 | 0.00000 | 0.00020 |
| 153| 3205.53 | 0.08241 | 0.67916 | 0.00000 | 0.00099 |
| 154| 3209.68 | 0.02694 | 0.07259 | 0.00000 | 0.00011 |
| 155| 3210.07 | 0.00176 | 0.00031 | 0.00000 | 0.00000 |
| 156| 3217.59 | 0.00396 | 0.00157 | 0.00000 | 0.00000 |
| 157| 3219.41 | 0.01217 | 0.01481 | 0.00000 | 0.00002 |
| 158| 3223.81 | 0.00562 | 0.00316 | 0.00000 | 0.00000 |
| 159| 3223.87 | 0.00528 | 0.00279 | 0.00000 | 0.00000 |
| 160| 3226.38 | 0.12815 | 1.64220 | 0.00000 | 0.00237 |
| 161| 3227.07 | 0.17646 | 3.11380 | 0.00000 | 0.00450 |
| 162| 3230.04 | 0.10602 | 1.12400 | 0.00000 | 0.00162 |
| 163| 3232.48 | 0.07911 | 0.62587 | 0.00000 | 0.00090 |
| 164| 3236.09 | 0.00361 | 0.00130 | 0.00000 | 0.00000 |
| 165| 3238.32 | 0.00471 | 0.00222 | 0.00000 | 0.00000 |
| 166| 3240.55 | 0.05662 | 0.32061 | 0.00000 | 0.00046 |
| 167| 3242.93 | 0.07953 | 0.63247 | 0.00000 | 0.00091 |
Method of calculating triplet energy of 55BT and Tc

The geometry of $^3(S_0T_1)$ of 55BT was optimized at the $U\omega B97X$-D/6-31G(d) level of theory assuming that 55BT belonged to the $C_1$ point group and then, its stability was confirmed using frequency analysis at the same level of theory. No imaginary modes were obtained, indicating that the optimized geometry was stationary minima. The geometry optimization and frequency analysis were performed using the Gaussian 16 package.\textsuperscript{1} The standard nuclear orientation and tube representation of the stable $^3(S_0T_1)$ geometry of 55BT are shown in Table S14 and Figure S3, respectively. From Figures S1 and S3, in the stable $^3(S_0T_1)$ geometry of 55BT, one of the Tc units has character of the optimized S0 geometry of the isolated Tc, whereas the other has character of the optimized T1 geometry of the isolated Tc. The T1 energy of 55BT was calculated by subtracting the SCF energy at the stable $^1(S_0S_0)$ geometry from the SCF energy at the stable $^3(S_0T_1)$ geometry. The SCF energy at the stable $^1(S_0S_0)$ geometry was calculated using the $\omega B97X$-D/6-31G(d) method. The SCF energy at the stable $^3(S_0T_1)$ geometry was calculated using the $U\omega B97X$-D/6-31G(d) method.

The standard nuclear orientation and tube representation of the stable T1 geometry of Tc are already shown in Table S6 and Figure S1, respectively. The T1 energy of Tc was calculated by subtracting the SCF energy at the stable S0 geometry from the SCF energy at the stable T1 geometry. The SCF energy at the stable S0 geometry was calculated using the $\omega B97X$-D/6-31G(d) method. The SCF energy at the stable T1 geometry was calculated using the $U\omega B97X$-D/6-31G(d) method. This method of calculating T1 energies of singlet fission molecules has been reported by Vallet \textit{et al.} and validated for predicting the T1 energy of Tc.\textsuperscript{5}
Table S14. Standard nuclear orientation of $^3(S_0T_1)$ geometry of 55BT optimized at the UωB97X-D/6-31G(d) level of theory assuming that 55BT belongs to the $C_1$ point group.

| Atom | Element symbol | x (Å)    | y (Å)    | z (Å)    |
|------|---------------|---------|---------|---------|
| 1    | C             | -0.544934 | 0.866952 | -0.532273 |
| 2    | C             | -0.471846 | 1.728388 | -1.628671 |
| 3    | C             | -1.514981 | 1.713799 | -2.624937 |
| 4    | C             | -2.583533 | 0.844544 | -2.484813 |
| 5    | C             | -2.680391 | -0.032199 | -1.389359 |
| 6    | C             | -1.641997 | -0.023770 | -0.391511 |
| 7    | C             | -1.750348 | -0.907768 | 0.700443 |
| 8    | C             | -2.823749 | -1.774484 | 0.834205  |
| 9    | C             | -3.862504 | -1.781522 | -0.165190 |
| 10   | C             | -3.766015 | -0.917608 | -1.243898 |
| 11   | C             | -4.963663 | -2.688622 | -0.004770 |
| 12   | C             | -5.028657 | -3.524277 | 1.065262  |
| 13   | C             | -3.996958 | -3.517741 | 2.058198  |
| 14   | C             | -2.936123 | -2.675419 | 1.946227  |
| 15   | C             | 0.620869  | 2.645284 | -1.805814 |
| 16   | C             | 0.672221  | 3.475499 | -2.880828 |
| 17   | C             | -0.362842 | 3.458783 | -3.868369 |
| 18   | C             | -1.415424 | 2.609280 | -3.743030 |
| 19   | H             | -3.369055 | 0.836576 | -3.237427 |
| 20   | H             | -0.970826 | -0.910267 | 1.456843 |
| 21   | H             | 4.546267  | -0.918497 | 2.002109 |
| 22   | H             | -5.745326 | -2.691525 | -0.760092 |
| 23   | H             | -5.866653 | -4.206032 | 1.175709 |
| 24   | H             | -4.070648 | -4.194625 | 2.904029 |
| 25   | H             | -2.150731 | -2.667183 | 2.697343 |
| 26   | H             | 1.409534  | 2.661281 | -1.060543 |
| 27   | H             | 1.506125  | 4.161446 | -2.997116 |
| 28   | H             | -0.299283 | 4.131149 | -4.718635 |
| 29   | H             | -2.206205 | 2.590008 | -4.488560 |
| 30   | C             | 0.522498  | 0.879124 | 0.505943 |
| 31   | C             | 0.377410  | 1.752708 | 1.655328 |
| 32   | C             | 1.389860  | 1.757418 | 2.655764 |
| 33   | C             | 2.528510  | 0.898672 | 2.501388 |
| 34   | C             | 2.681501  | 0.051800 | 1.402026 |
| 35   | C             | 1.645797  | 0.037579 | 0.367865 |
| 36   | C             | 1.808634  | -0.816362 | -0.722590 |
| 37   | C             | 2.950387  | -1.676091 | -0.867171 |
| 38   | C             | 3.956894  | -1.660246 | 0.136925 |
| 39   | C             | 3.790916  | -0.783394 | 1.259868 |
| 40   | C             | 5.071525  | -2.496753 | -0.00368 |
| 41   | C             | 5.200283  | -3.335550 | -1.101612 |
|   |   |        |        |        |
|---|---|--------|--------|--------|
| 42 | C | 4.212851 | -3.351302 | -2.086568 |
| 43 | C | 3.098619 | -2.527772 | -1.967975 |
| 44 | C | -0.730502 | 2.592958  | 1.813917  |
| 45 | C | -0.848736 | 3.420977  | 2.927147  |
| 46 | C | 0.141974  | 3.424648  | 3.904767  |
| 47 | C | 1.252038  | 2.597516  | 3.766187  |
| 48 | H | 3.296239  | 0.910782  | 3.271445  |
| 49 | H | 1.048457  | -0.839210 | -1.497468 |
| 50 | H | 4.560208  | -0.772374 | 2.028607  |
| 51 | H | 5.840445  | -2.483918 | 0.768057  |
| 52 | H | 6.070628  | -3.978248 | -1.193019 |
| 53 | H | 4.312243  | -4.006240 | -2.946777 |
| 54 | H | 2.327794  | -2.538692 | -2.734256 |
| 55 | H | -1.506865 | 2.596344  | 1.055654  |
| 56 | H | -1.718080 | 4.063404  | 3.027982  |
| 57 | H | 0.051712  | 4.069590  | 4.773532  |
| 58 | H | 2.029067  | 2.596238  | 4.526528  |
Figure S3. The stable $^3(S_0T_1)$ geometry of 55BT. Geometry optimization was done using the \Uomega\B97X-D/6-31G(d) method. All the H atoms are omitted for clarity. Numbers are representative C–C bond-lengths (Å) and the torsion angle between the tetracene units (degree).

Figure S4. HOMO, LUMO, HOMO−1, and LUMO+1 at the stable $^1(S_0S_1)$ geometry calculated using the RAS(4,4)-2SF/6-31G(d) method.
Figure S5. The spatial overlap $\rho$ distribution between the electronic wave functions of $^1(S_0S_1)$ and $^1(T_1T_1)$ at the stable $^1(S_0S_1)$ geometry calculated using the RAS(4,4)-2SF/6-31G(d) method.
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