Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Quasi-intrinsic fluorescent probes for detecting DNA adduct (^{ABP}dG) based on excited-state intermolecular charge transfer mechanism

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Fig. S1. FMOs involved in the absorption/emission processes of ^{ABP}G (left panel) and ^{ABP}G:C (right panel).

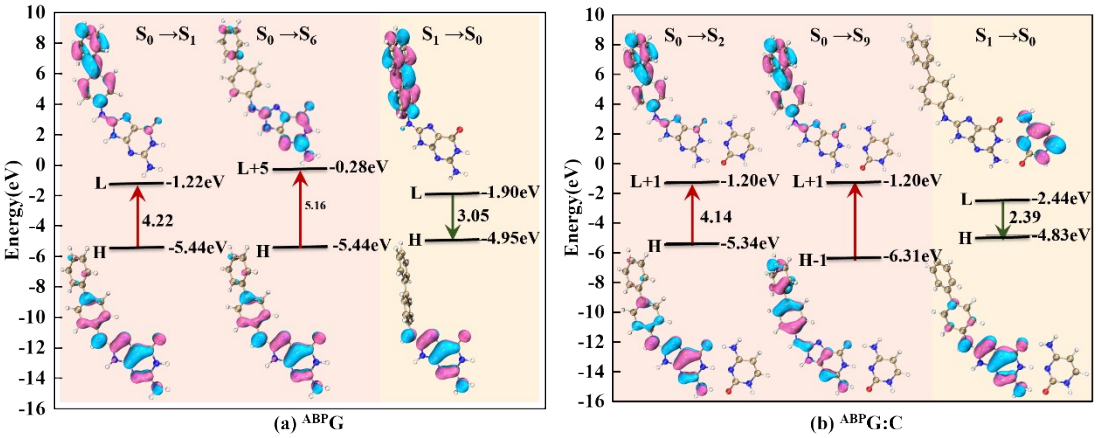
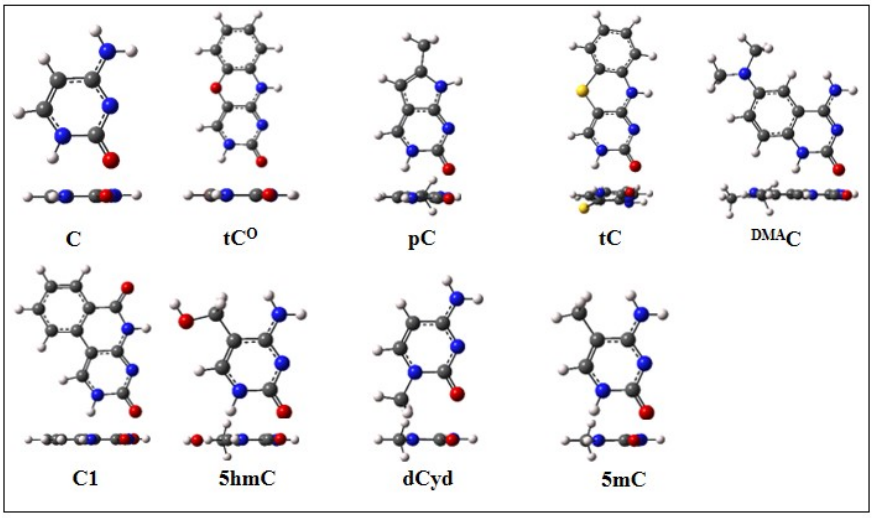


Table S1. Absorption/fluorescence wavelengths (λ), corresponding oscillator strengths ($f_{abs.}$ and $f_{flu.}$), and state assignments for ^{ABP}G and ^{ABP}G:C.

Optical spectral	Base	Transition	λ(nm)	$f_{abs.}/f_{flu.}$	Assignment(CI/Type/Gap(eV))
Absorption	^{ABP}G	$S_0 \rightarrow S_1$	330	0.85	H→L(98.2%/ππ*/4.22)
		$S_0 \rightarrow S_6$	266	0.36	H→L+5(51.2%/ππ*/5.16)
	^{ABP}G:C	$S_0 \rightarrow S_2$	337	0.79	H→L+1(98.2%/ππ*/4.14)
		$S_0 \rightarrow S_9$	265	0.43	H-1→L+1(70.8%/ππ*/5.11)
Fluorescence	^{ABP}G	$S_1 \rightarrow S_0$	490	0	L→H(99.0%/ππ*/3.05)
	^{ABP}G:C	$S_1 \rightarrow S_0$	632	0	L→H(99.7%/ππ*/2.39)

Fig. S2. Optimized structures of monomers.

(a) C and C-analogues in S_0 state



(b) C and C-analogues in S_1 state

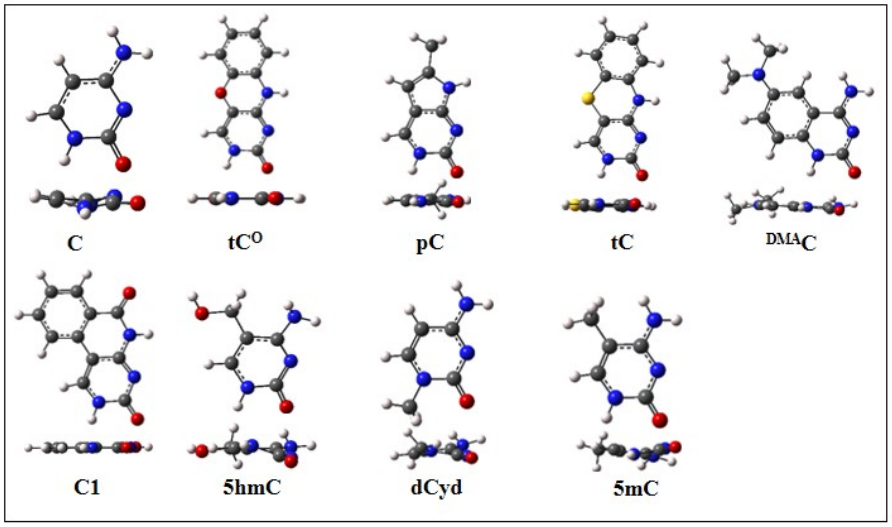


Table S2. The structure coordinates for monomers optimized with B3LYP-D3/6-311++G(d,p).

C (S_0)

	X	Y	Z
C	-0.19921	1.70859	0.00016
C	1.04948	1.18030	-0.00020
C	1.13881	-0.25271	-0.00023
C	-1.18037	-0.51209	0.00004
H	-2.21708	1.27665	0.00044
H	-0.39464	2.77269	0.00048
H	1.92809	1.80826	-0.00056
N	2.35086	-0.84246	-0.00355
H	3.20195	-0.30532	0.01319
H	2.41331	-1.84863	0.01024
N	0.07016	-1.04806	0.00006
N	-1.28298	0.89053	0.00023
O	-2.21878	-1.18101	0.00004

C (S_1)

	X	Y	Z
C	-0.29255	1.72881	0.08012
C	1.01002	1.19065	0.11242
C	1.17812	-0.18480	0.00512
C	-1.11677	-0.51956	0.00678
H	-2.25934	1.14953	-0.40289
H	-0.53992	2.76995	0.20537
H	1.86012	1.85292	0.22939
N	2.38146	-0.82554	-0.21263
H	3.21361	-0.26510	-0.08693
H	2.45574	-1.74414	0.20685
N	0.07492	-1.03843	0.19745
N	-1.31580	0.83711	-0.21825
O	-2.17341	-1.23320	0.03193

tC^{O} (S_0)

		X	Y	Z			X	Y	Z
1	C	1.91557	1.59498	0.00024	12	H	3.97766	1.48966	0.00058
2	C	0.78118	0.85907	-0.00015	13	H	1.91793	2.67570	0.00034
3	C	0.92727	-0.56822	-0.00010	14	H	-0.11321	-2.31843	-0.00046
4	C	3.25425	-0.43950	0.00019	15	H	-4.94603	1.01853	0.00073
5	C	-1.48191	-0.72267	-0.00025	16	H	-4.79308	-1.46673	0.00072
6	C	-1.57893	0.67491	-0.00024	17	H	-2.57085	-2.56854	0.00007
7	C	-2.81636	1.29962	0.00011	18	N	3.12214	0.95149	0.00036
8	H	-2.85379	2.38209	0.00009	19	N	2.09761	-1.17529	-0.00000
9	C	-3.98028	0.52832	0.00046	20	N	-0.20718	-1.31148	-0.00064
10	C	-3.89434	-0.86239	0.00046	21	O	4.37974	-0.94311	0.00023
11	C	-2.64694	-1.48711	0.00008	22	O	-0.45269	1.47719	-0.00084

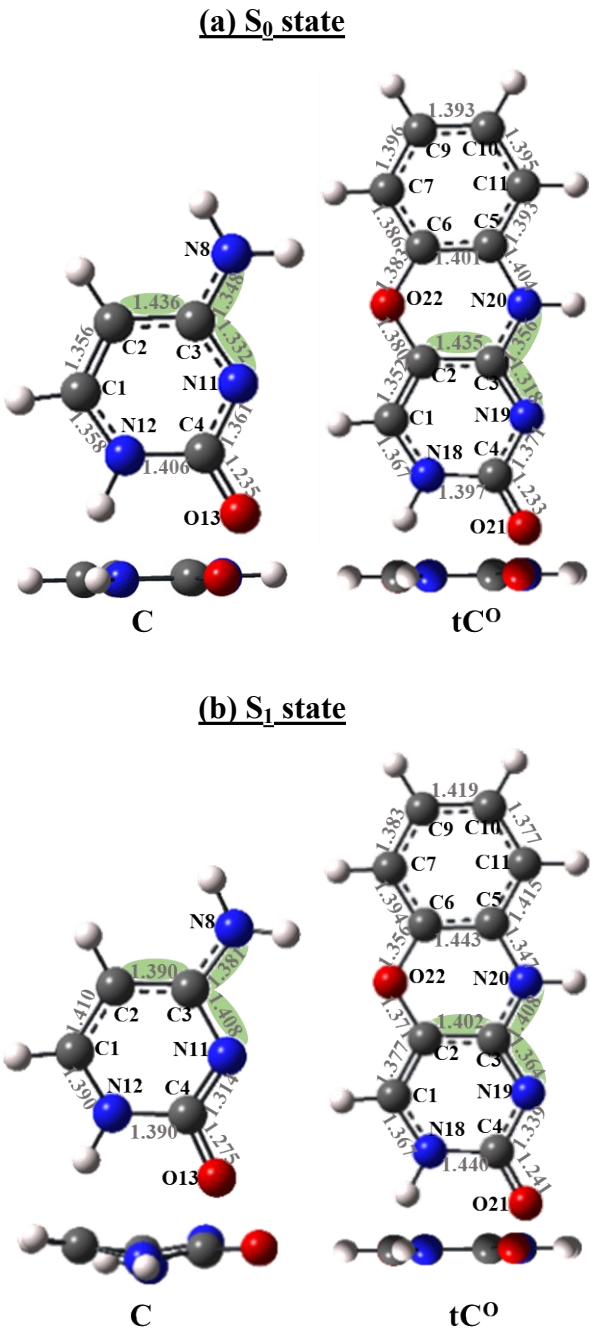
tC^{O} (S_1)

		X	Y	Z			X	Y	Z
1	C	1.90557	1.62735	-0.00001	12	H	3.96885	1.48791	0.00009
2	C	0.78200	0.83096	-0.00005	13	H	1.88496	2.70670	0.00012
3	C	0.92235	-0.56416	0.00006	14	H	-0.15407	-2.34703	-0.00014
4	C	3.23761	-0.46693	-0.00038	15	H	-4.91819	1.07395	0.00027
5	C	-1.47170	-0.76535	-0.00003	16	H	-4.80742	-1.41392	0.00005
6	C	-1.55744	0.67516	0.00007	17	H	-2.63524	-2.58190	-0.00014
7	C	-2.79161	1.32373	0.00018	18	N	3.10268	0.96708	-0.00002
8	H	-2.80479	2.40637	0.00026	19	N	2.12374	-1.21087	-0.00012
9	C	-3.95644	0.57801	0.00018	20	N	-0.25273	-1.33961	-0.00011
10	C	-3.88938	-0.83924	0.00005	21	O	4.39906	-0.90281	0.00014
11	C	-2.68152	-1.49967	-0.00004	22	O	-0.44238	1.44689	-0.00000

Table S3. Absorption/fluorescence wavelengths (λ) and corresponding oscillator strengths ($f_{abs.}$ and $f_{flu.}$) of monomers.

	Abs. (nm)/$f_{abs.}$			Flu. (nm)/$f_{flu.}$
C	257/0.08	227/0.14	203/0.18	337/0.06
tC^{O}	354/0.14	271/0.35		445/0.24
pC	341/0.08	229/0.34	214/0.07	448/0.10
tC	362/0.07	281/0.24	243/0.12	488/0.12
^{DMA}C	396/0.08	246/0.05		503/0.12
C1	331/0.16	261/0.49		377/0.31
5hmC	264/0.08	225/0.14	203/0.38	339/0.09
dCyd	260/0.13	229/0.14	207/0.16	336/0.10
5mC	265/0.09	226/0.14	203/0.35	337/0.10

Fig. S3. Optimized geometries and side-view graphs of C and tC^O in water. The Δd (Å) is located around the C3 of the 6-membered ring (green underpainting in structure chart), which denotes the maximum difference of some important bond lengths between natural base and its analogues.



I. Calculation details of the binding energy:

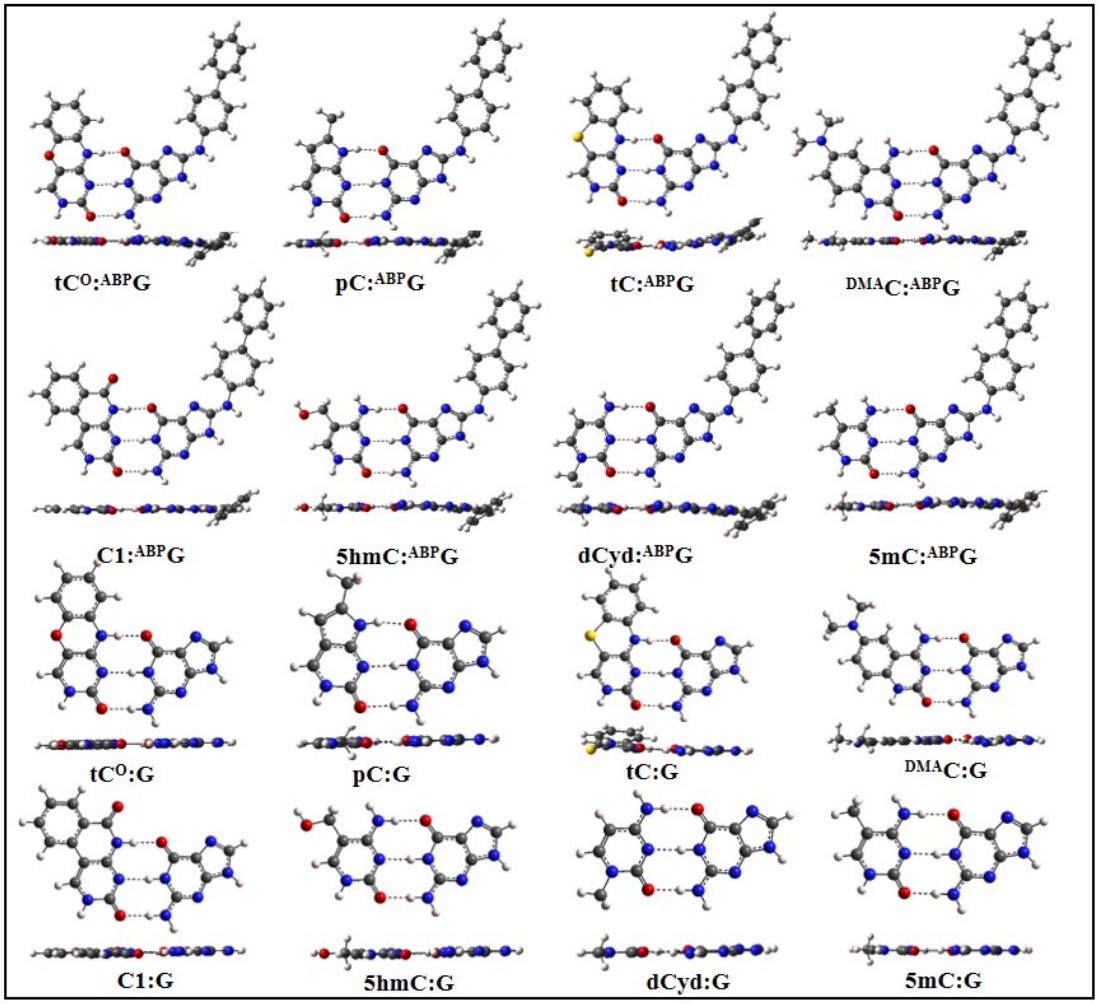
The intermolecular binding energy ΔE of Watson-Crick (WC) base pair was calculated to evaluate the stability of base pair, which is defined as the energy differences between the complex (E_{AB}) and the individual bases (E_A and E_B)

$$\Delta E = E_{AB} - (E_A + E_B) + E_{BSSE}. \quad (1)$$

Herein, the binding energies of all considered base pairs are corrected for basis set superposition error (BSSE) using the counterpoise correction method.

Fig. S4. Optimized structures of base pairs.

(a) Base pairs in S_0 state



(b) Base pairs in S_1 state

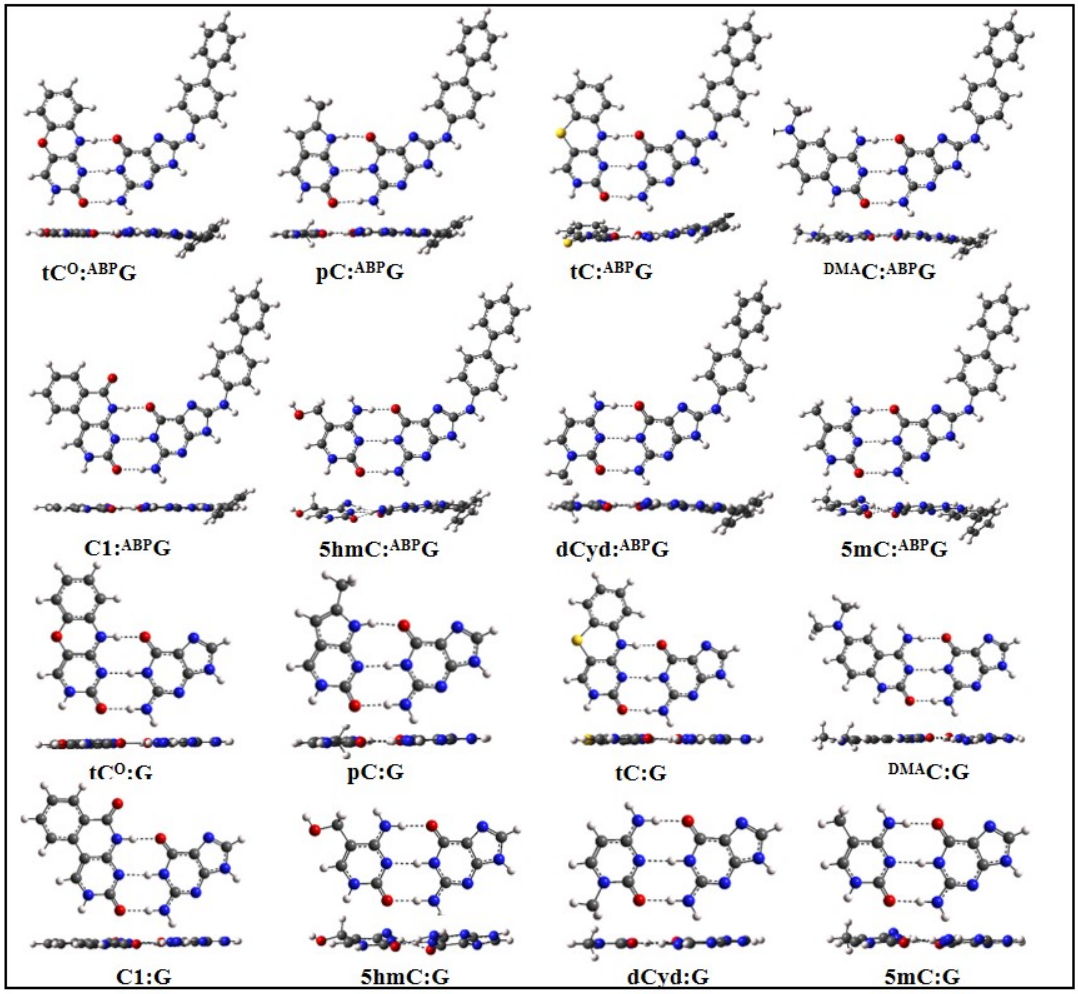


Table S4. The structures coordinates for base pairs optimized with B3LYP-D3/6-311++G(d,p).

tC^{O}:^{ABP}G (S_0)

		X	Y	Z			X	Y	Z
1	C	-0.03318	-1.97925	0.01285	31	H	4.86657	1.56510	0.01473
2	C	-0.10144	-3.37130	0.01801	32	H	8.84430	-0.02496	1.27600
3	C	-2.32670	-3.47228	0.02849	33	H	10.67953	1.61493	1.24338
4	C	-1.24897	-1.25412	0.01149	34	H	10.45801	3.71848	-0.06295
5	C	1.99859	-2.64885	0.00591	35	H	8.37533	4.14528	-1.35148
6	H	-3.29003	-1.62968	0.00218	36	H	6.55303	2.49014	-1.34934
7	H	1.51343	-4.75468	0.01531	37	N	3.36207	-2.78233	0.00030
8	O	-1.41050	-0.01539	0.00377	38	H	3.70948	-3.73003	0.00141
9	N	1.29005	-1.54455	0.00541	39	C	-7.37603	0.55498	-0.06832
10	N	1.20599	-3.79247	0.01359	40	C	-6.24691	1.29712	-0.02100
11	N	-1.18991	-4.15859	0.02570	41	C	-4.99315	0.59819	-0.01880
12	N	-2.36760	-2.10108	0.01838	42	C	-6.06161	-1.48282	-0.10678
13	N	-3.50967	-4.11959	0.06147	43	C	-3.88631	2.71732	0.06948
14	H	-4.40230	-3.62893	-0.03304	44	C	-5.12196	3.37671	0.06778
15	H	-3.49060	-5.12301	-0.02174	45	C	-5.18986	4.76009	0.11127
16	C	6.45526	0.11197	-0.02539	46	H	-6.16253	5.23662	0.10835
17	C	6.71699	-1.26856	-0.03016	47	C	-4.01020	5.50655	0.15772
18	C	5.68912	-2.19882	-0.02268	48	C	-2.77508	4.86091	0.15988
19	C	4.34602	-1.78441	-0.00795	49	C	-2.71260	3.46802	0.11584
20	C	4.06603	-0.41028	-0.00176	50	H	-8.11273	-1.37722	-0.14783
21	C	5.11189	0.50930	-0.01109	51	H	-8.36604	0.98754	-0.07504
22	C	7.55676	1.10491	-0.03531	52	H	-2.94899	0.81461	0.02024
23	C	8.74116	0.87819	0.68522	53	H	-4.06380	6.58776	0.19183
24	C	9.77745	1.80965	0.67388	54	H	-1.85775	5.43566	0.19585
25	C	9.65257	2.99296	-0.05515	55	H	-1.75925	2.95230	0.11720
26	C	8.48107	3.23325	-0.77440	56	N	-7.27553	-0.81191	-0.11095
27	C	7.44679	2.29958	-0.76609	57	N	-4.92638	-0.72770	-0.05896
28	H	7.74056	-1.62362	-0.06242	58	N	-3.85704	1.31533	0.02496
29	H	5.92576	-3.25781	-0.03764	59	O	-6.03950	-2.72218	-0.14586
30	H	3.04117	-0.07352	0.01855	60	O	-6.31389	2.67274	0.02201

tC^{O}:^{ABP}G (S_1)

		X	Y	Z			X	Y	Z
1	C	-0.03297	-1.96692	0.02857	31	H	-4.84989	1.596075	-0.02570
2	C	0.05603	-3.39023	0.00166	32	H	-8.82262	0.02080	-1.29776
3	C	2.28935	-3.39728	0.01800	33	H	10.64658	1.67460	-1.27304
4	C	1.19851	-1.20816	0.04200	34	H	10.41944	3.76923	0.04456
5	C	-2.03805	-2.67907	0.00513	35	H	-8.34451	4.17961	1.34880
6	H	3.27665	-1.53580	0.01039	36	H	-6.52885	2.51635	1.34712
7	H	-1.55284	-4.77743	-0.03051	37	N	-3.37330	-2.76728	-0.00308
8	O	1.28740	0.01766	0.05573	38	H	-3.74794	-3.70815	-0.01629
9	N	-1.30857	-1.55003	0.03044	39	C	7.36079	0.40571	0.09974
10	N	-1.24600	-3.81408	-0.01330	40	C	6.24024	1.17124	-0.12157
11	N	1.14214	-4.12472	-0.00418	41	C	4.99010	0.57755	-0.19891
12	N	2.32324	-2.02743	0.03265	42	C	5.88466	-1.56096	0.14727
13	N	3.44107	-4.04496	0.02532	43	C	3.96679	2.73457	-0.23727
14	H	4.37034	-3.55473	0.10292	44	C	5.24807	3.31281	-0.14519
15	H	3.39791	-5.05361	0.02033	45	C	5.40261	4.67656	0.05459
16	C	-6.44251	0.14384	0.01695	46	H	6.40650	5.07993	0.12076
17	C	-6.71482	-1.23331	0.02362	47	C	4.27960	5.50306	0.15861
18	C	-5.69026	-2.16707	0.01758	48	C	3.00513	4.94350	0.07116
19	C	-4.35249	-1.74794	0.00428	49	C	2.85083	3.56997	-0.11977
20	C	-4.05699	-0.37982	-0.00404	50	H	7.91377	-1.61073	0.35793
21	C	-5.09674	0.54160	0.00264	51	H	8.36565	0.77847	0.18869
22	C	-7.53784	1.14250	0.02407	52	H	2.95971	0.93271	-0.24892
23	C	-8.71800	0.92163	-0.70401	53	H	4.40624	6.56840	0.30850
24	C	-9.74714	1.86035	-0.69690	54	H	2.12572	5.57168	0.15430
25	C	-9.61839	3.03896	0.03889	55	H	1.86105	3.13117	-0.18569
26	C	-8.45100	3.27077	0.76733	56	N	7.13787	-0.98399	0.21928
27	C	-7.42108	2.33294	0.75956	57	N	4.80325	-0.79121	-0.04975
28	H	-7.73961	-1.58233	0.05597	58	N	3.85715	1.36260	-0.45780
29	H	-5.92892	-3.22496	0.03280	59	O	5.81338	-2.81977	0.27628
30	H	-3.03211	-0.04468	-0.02425	60	O	6.39486	2.54715	-0.30355

tC^{O}:G (S_0)

		X	Y	Z			X	Y	Z
1	C	3.44567	-1.38564	0.00030	20	C	-2.65061	-1.33628	-0.00069
2	C	4.49041	-0.45666	-0.00014	21	C	-3.93739	-0.78365	-0.00064
3	C	3.16741	1.33657	-0.00100	22	C	-5.05993	-1.59612	-0.00005
4	C	2.11100	-0.89303	0.00027	23	H	-6.03987	-1.13479	-0.00003
5	C	5.24027	-2.53795	0.00083	24	C	-4.90549	-2.98433	0.00045
6	H	1.12413	0.92875	-0.00030	25	C	-3.62955	-3.54500	0.00042
7	H	6.57920	-0.86557	0.00005	26	C	-2.50301	-2.72231	-0.00012
8	H	5.96499	-3.33772	0.00117	27	H	-2.09382	4.52582	0.00246
9	O	1.05134	-1.54634	0.00074	28	H	-4.09823	3.24612	0.00126
10	N	3.93945	-2.68102	0.00090	29	H	-0.58098	-0.87627	-0.00088
11	N	5.63097	-1.21379	0.00022	30	H	-5.78321	-3.61886	0.00088
12	N	4.41523	0.88701	-0.00075	31	H	-3.50498	-4.62090	0.00084
13	N	2.07027	0.50557	-0.00024	32	H	-1.50457	-3.14415	-0.00014
14	N	2.92252	2.65987	-0.00239	33	N	-2.01227	3.51827	0.00152
15	H	1.97520	3.04709	-0.00052	34	N	-0.60978	1.63123	-0.00009
16	C	-3.14247	2.74210	0.00091	35	N	-1.53770	-0.48176	-0.00131
17	C	-3.01627	1.39589	-0.00024	36	O	0.25088	3.74895	0.00153
18	C	-1.68703	0.85438	-0.00055	37	O	-4.13216	0.58760	-0.00140
19	C	-0.73018	2.99018	0.00099	38	H	3.71394	3.28230	-0.00104

tC^{O}:G (S_1)

		X	Y	Z			X	Y	Z
1	C	3.44528	-1.38480	0.00036	20	C	2.60733	-1.34637	-0.00014
2	C	4.48452	-0.44957	-0.00034	21	C	3.92671	-0.75822	-0.00004
3	C	3.14795	1.33378	-0.00139	22	C	5.07134	-1.55313	-0.00019
4	C	2.10814	-0.89882	0.00024	23	H	6.03860	-1.06650	-0.00011
5	C	5.24707	-2.52639	0.00101	24	C	4.94666	-2.93122	-0.00043
6	H	1.10126	0.92067	-0.00056	25	C	3.65851	-3.52666	-0.00049
7	H	6.57606	-0.84627	-0.00044	26	C	2.51542	-2.76022	-0.00035
8	H	5.97645	-3.32192	0.00148	27	H	2.07367	4.51512	0.00136
9	O	1.05335	-1.56319	0.00085	28	H	4.12091	3.23908	0.00100
10	N	3.94698	-2.67727	0.00112	29	H	0.56633	-0.93274	0.00018
11	N	5.62995	-1.20006	-0.00004	30	H	5.83081	-3.55520	-0.00056
12	N	4.40022	0.89299	-0.00122	31	H	3.57380	-4.60650	-0.00066
13	N	2.05586	0.49731	-0.00064	32	H	1.53207	-3.21418	-0.00040
14	N	2.89673	2.65613	-0.00271	33	N	2.01472	3.50590	0.00107
15	H	1.94748	3.04399	-0.00115	34	N	0.56170	1.62910	0.00018
16	C	3.15873	2.75020	0.00085	35	N	1.52850	-0.54382	-0.00005
17	C	2.98060	1.38480	0.00044	36	O	0.24628	3.76887	0.00079
18	C	1.68885	0.85044	0.00015	37	O	4.09782	0.58913	0.00030
19	C	0.70218	2.96016	0.00067	38	H	3.68696	3.28013	-0.00173

Table S5. Absorption/fluorescence wavelengths (λ) and corresponding oscillator strengths ($f_{abs.}$ and $f_{flu.}$) of base pairs.

	Abs. (nm)/$f_{abs.}$				Flu. (nm)/$f_{flu.}$	
	Base pairing with ^{ABP}G		Base pairing with G		Base pairing with ^{ABP}G	Base pairing with G
C	337/0.79	265/0.43	265/0.12	246/0.29	632/0	840/0
tC^{O}	336/0.80		362/0.15	271/0.27	662/0	462/0.27
pC	337/0.73	268/0.54	345/0.08	244/0.31	657/0	469/0.09
tC	335/0.80		375/0.08	281/0.22	505/0.15	506/0.15
^{DMA}C	337/0.80		400/0.09	269/0.19	503/0.12	504/0.12
C1	335/0.81		328/0.15	262/0.47	778/0	598/0
5hmC	337/0.78	268/0.49	265/0.13	245/0.26	628/0	513/0
dCyd	337/0.78	265/0.29	258/0.16	245/0.30	619/0	815/0
5mC	337/0.77	267/0.52	265/0.13	245/0.36	615/0	809/0

Fig. S5. Absorption spectra of base pairs (tC^{O}:^{ABP}G, tC^{O}:G) in water solution.

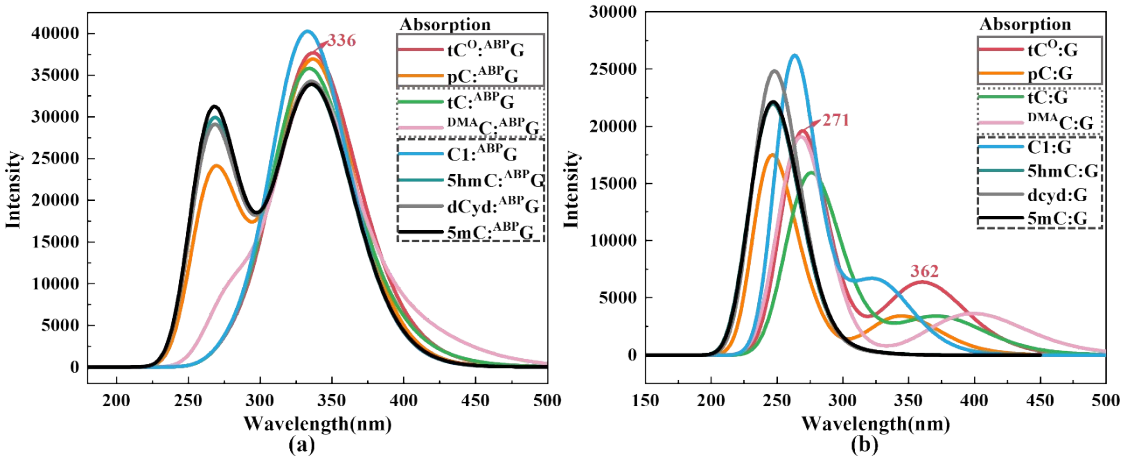


Fig. S6. FMOs involved in the absorption and emission processes of tC:^{ABP}G (upper left), tC:G (upper right), C1:^{ABP}G (lower left), C1:G (lower right).

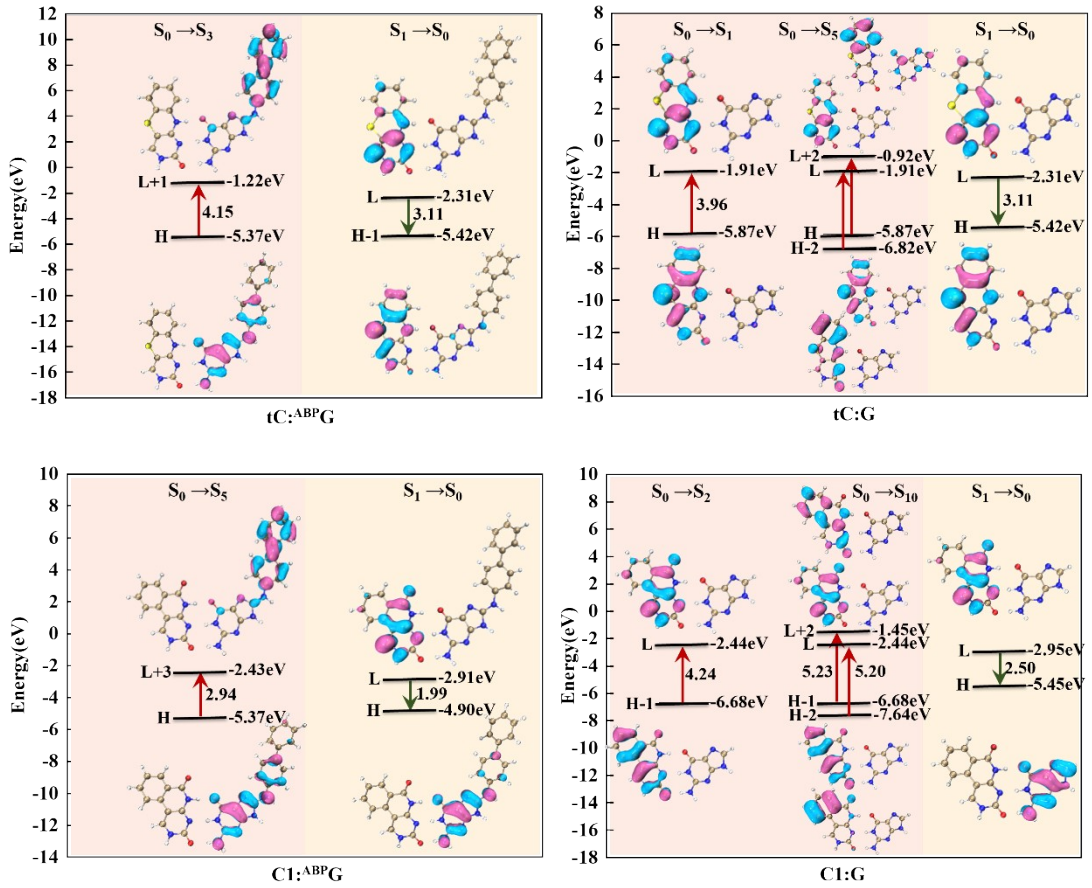


Table S6. Absorption/fluorescence wavelengths (λ), corresponding oscillator strengths ($f_{abs.}$ and $f_{flu.}$), and state assignments for tC:^{ABP}G, tC:G, C1:^{ABP}G, C1:G.

Optical spectral	Base pair	Transition	λ(nm)	$f_{abs.}/f_{flu.}$	Assignment(CI/Type/Gap(eV))
Absorption	tC:^{ABP}G	$S_0 \rightarrow S_3$	335	0.80	H→L+1(98.2%/ππ*/4.15)
	tC:G	$S_0 \rightarrow S_1$	375	0.08	H→L(94.5%/ππ*/3.96)
		$S_0 \rightarrow S_5$	281	0.22	H-2→L(57.8%/ππ*/4.91)
					H→L+2(30.6%/ππ*/4.95)
	C1:^{ABP}G	$S_0 \rightarrow S_5$	335	0.81	H→L+3(97.1%/ππ*/2.94)
	C1:G	$S_0 \rightarrow S_2$	328	0.15	H-1→L(95.4%/ππ*/4.24)
		$S_0 \rightarrow S_{10}$	262	0.47	H-1→L+2(50.5%/ππ*/5.23)
					H-2→L(25.8%/ππ*/5.20)
Fluorescence	tC:^{ABP}G	$S_1 \rightarrow S_0$	505	0.15	L→H-1(76.3%/ππ*/3.11)
	tC:G	$S_1 \rightarrow S_0$	506	0.15	L→H(98.8%/ππ*/3.11)
	C1:^{ABP}G	$S_1 \rightarrow S_0$	778	0	L→H(99.7%/ππ*/1.99)
	C1:G	$S_1 \rightarrow S_0$	598	0	L→H(99.9%/ππ*/2.50)

Fig. S7. Fluorescence spectra of monomer (tC^{O}) (left panel) and related base pairs [tC^{O}:^{ABP}G (dotted line), tC^{O}:G (solid line) right panel] determined by three functional (PBE0, wB97XD, CAM-B3LYP) with 6-311++G(d,p) basis set in water solution.

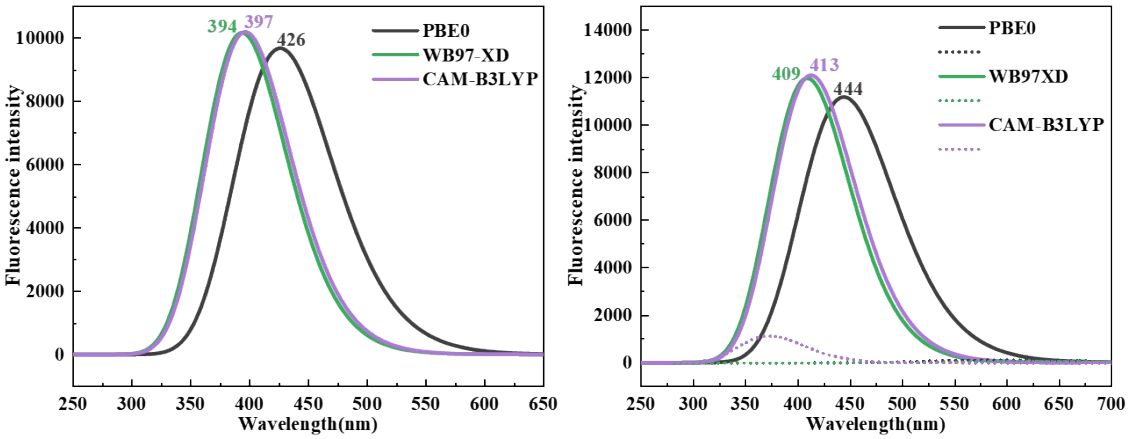


Fig. S8. FMOs involved in the emission processes of tC^{O} (left panel), tC^{O}:G (middle panel), tC^{O}:^{ABP}G (right panel) determined by wB97XD functional with 6-311++G(d,p) basis set in water solution.

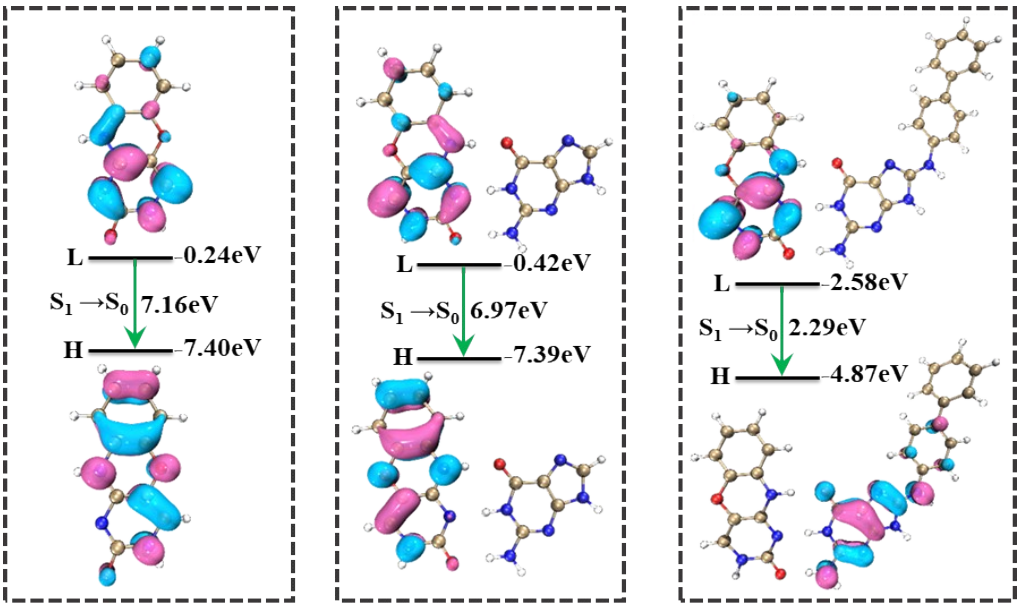


Fig. S9. Fluorescence spectra of monomer (tC^{O}) and related base pairs (tC^{O}:^{ABP}G, tC^{O}:G) in continuum with a low dielectric constant (ε~4).

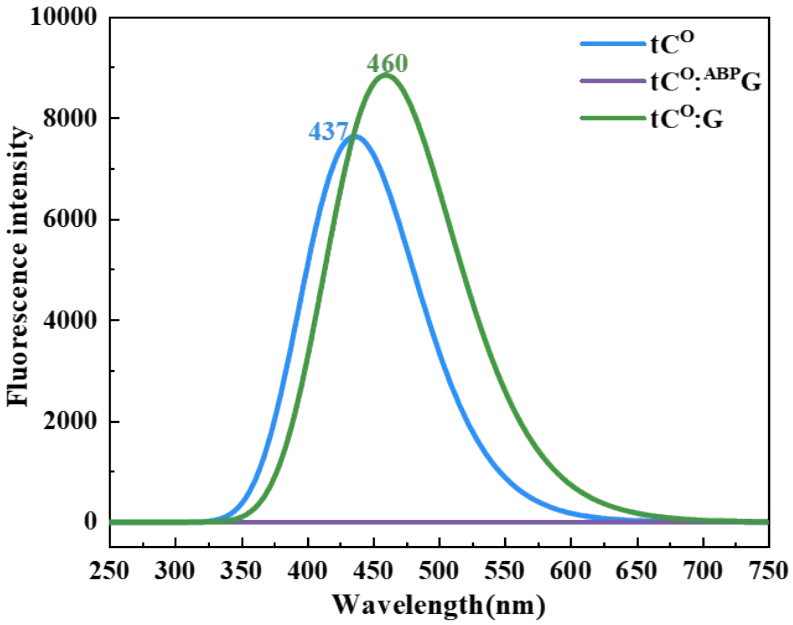


Fig. S10. FMOs involved in the emission processes of monomer (tC^{O}) and related base pairs (tC^{O}:^{ABP}G, tC^{O}:G) in continuum with a low dielectric constant (ε~4).

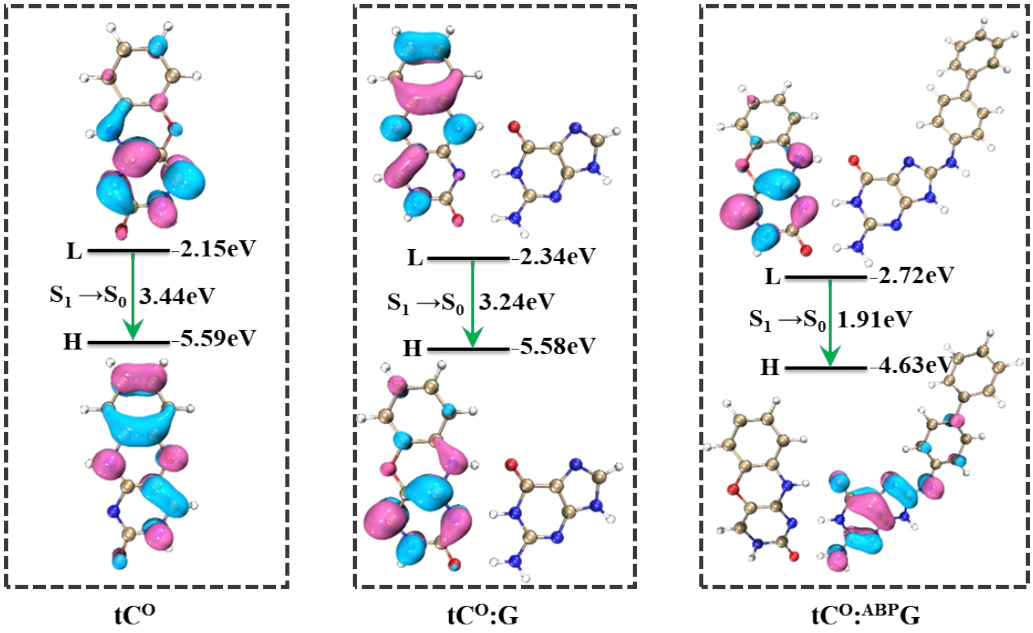


Table S7. The structures coordinates for monomers and base pairs of linking to deoxyribose optimized with B3LYP-D3/6-311++G(d,p).

dtC^{O} (S_0)

		X	Y	Z			X	Y	Z
1	C	0.30401	-0.09169	0.01485	20	O	1.32524	3.29888	-0.15931
2	C	-1.03825	0.05016	0.04072	21	O	-1.85521	-1.06066	0.13708
3	C	-1.55999	1.37960	-0.04248	22	H	2.02179	-3.50838	0.33069
4	C	0.57623	2.31999	-0.12042	23	O	2.36043	-2.60683	0.33311
5	C	-3.77378	0.42356	0.00299	24	C	3.34659	-2.48172	-0.69910
6	C	-3.22227	-0.86189	0.09114	25	H	2.91151	-2.70575	-1.67919
7	C	-4.03960	-1.98071	0.14247	26	H	4.18413	-3.16703	-0.52247
8	H	-3.57957	-2.95896	0.21036	27	C	3.88029	-1.06021	-0.71749
9	C	-5.42692	-1.82703	0.10754	28	H	4.69732	-1.01463	-1.44268
10	C	-5.98457	-0.55305	0.01983	29	O	2.84802	-0.14366	-1.14759
11	C	-5.15914	0.57029	-0.03302	30	C	2.56498	0.81622	-0.12915
12	H	0.79501	-1.05631	0.05080	31	H	2.98862	1.78187	-0.39571
13	H	-3.28334	2.46499	-0.11427	32	C	4.37701	-0.53667	0.63918
14	H	-6.06279	-2.70279	0.14867	33	H	4.65705	-1.35406	1.30860
15	H	-7.05983	-0.42646	-0.00812	34	C	3.17968	0.25770	1.15883
16	H	-5.58446	1.56513	-0.10168	35	H	2.47988	-0.41892	1.65092
17	N	1.11189	1.01570	-0.07139	36	H	3.46283	1.04626	1.85651
18	N	-0.78853	2.44303	-0.11845	37	O	5.50975	0.30294	0.37310
19	N	-2.90867	1.52822	-0.04545	38	H	5.81756	0.67375	1.20816

dtC^{O} (S_1)

		X	Y	Z			X	Y	Z
1	C	0.30855	-0.11618	0.01592	20	O	1.33876	3.28978	-0.23701
2	C	-1.05207	0.07550	0.01114	21	O	-1.85506	-1.03383	0.07628
3	C	-1.57273	1.37298	-0.07478	22	H	2.05985	-3.53702	0.14272
4	C	0.53523	2.35068	-0.15923	23	O	2.38931	-2.63476	0.21177
5	C	-3.78801	0.45330	0.00721	24	C	3.40091	-2.43658	-0.78412
6	C	-3.20107	-0.86214	0.07311	25	H	2.99572	-2.61072	-1.78698
7	C	-3.99789	-2.00389	0.14382	26	H	4.24337	-3.12002	-0.62291
8	H	-3.51112	-2.96984	0.19323	27	C	3.91487	-1.00892	-0.70948
9	C	-5.37574	-1.87829	0.14901	28	H	4.75997	-0.91981	-1.39837
10	C	-5.96855	-0.59165	0.08473	29	O	2.89199	-0.08205	-1.13016
11	C	-5.19980	0.54882	0.01588	30	C	2.54655	0.82103	-0.06534
12	H	0.77993	-1.08976	0.03637	31	H	2.97208	1.80199	-0.26084
13	H	-3.34648	2.46203	-0.10344	32	C	4.35504	-0.55498	0.69111
14	H	-6.00051	-2.76022	0.20224	33	H	4.62457	-1.40455	1.32438
15	H	-7.04806	-0.50341	0.08969	34	C	3.12905	0.19314	1.21005
16	H	-5.65728	1.52955	-0.03322	35	H	2.42265	-0.51773	1.64038
17	N	1.10329	1.00057	-0.04957	36	H	3.37765	0.94620	1.95860
18	N	-0.79465	2.48383	-0.16063	37	O	5.48491	0.31271	0.51392
19	N	-2.96977	1.52339	-0.06022	38	H	5.75036	0.64715	1.37838

dtC^{O}:^{ABP}dG (S_0)

		X	Y	Z			X	Y	Z
1	C	-1.20154	-0.78431	-0.15374	47	C	2.19614	5.74192	-0.58047
2	C	-1.27176	-2.17066	-0.08522	48	C	1.99666	4.36655	-0.45959
3	C	0.93482	-2.48664	-0.03370	49	H	7.37321	1.37368	0.03445
4	C	0.07857	-0.17917	-0.15652	50	H	1.96851	1.71281	-0.20978
5	C	-3.29627	-1.24699	-0.17525	51	H	3.64865	7.33120	-0.67358
6	H	2.07454	-0.74744	-0.07056	52	H	1.34051	6.39933	-0.67472
7	O	0.35702	1.03803	-0.20575	53	H	0.99768	3.94589	-0.45870
8	N	-2.47226	-0.22632	-0.21898	54	N	6.13840	-0.32369	0.11963
9	N	-2.62035	-2.47755	-0.08358	55	N	3.79520	-0.00407	0.00228
10	N	-0.26385	-3.05639	-0.02352	56	N	2.92095	2.12248	-0.21381
11	N	1.11080	-1.12740	-0.09247	57	O	4.67813	-2.09059	0.20001
12	N	2.04809	-3.24791	-0.00590	58	O	5.49970	3.23439	-0.21817
13	H	2.98152	-2.83988	0.09118	59	H	-7.46610	-3.06955	-0.95605
14	H	1.92737	-4.23774	0.13492	60	O	-6.64874	-3.42276	-0.58819
15	C	-7.28573	2.10513	0.18368	61	C	-6.28965	-4.60650	-1.31545
16	C	-7.70380	0.78417	0.41490	62	H	-6.22044	-4.39209	-2.38663
17	C	-6.82515	-0.28298	0.29963	63	H	-7.03069	-5.39819	-1.15908
18	C	-5.48503	-0.07540	-0.07149	64	C	-4.94211	-5.08198	-0.81541
19	C	-5.05177	1.23876	-0.30147	65	H	-4.68706	-6.01423	-1.32831
20	C	-5.94364	2.29991	-0.16896	66	O	-3.95501	-4.07817	-1.13609
21	C	-8.22574	3.24478	0.31236	67	C	-3.14537	-3.82188	0.01379
22	C	-9.56330	3.12795	-0.10079	68	H	-2.27206	-4.47820	0.01634
23	C	10.44766	4.19800	0.01981	69	C	-4.85680	-5.31933	0.70928
24	C	10.01451	5.41262	0.55316	70	H	-5.84954	-5.36728	1.16260
25	C	-8.68826	5.54439	0.96689	71	C	-4.04712	-4.12258	1.21482
26	C	-7.80538	4.47278	0.84969	72	H	-4.70835	-3.28277	1.42890
27	H	-8.72416	0.58813	0.72419	73	H	-3.47278	-4.35331	2.11207
28	H	-7.16564	-1.28475	0.52886	74	O	-4.16311	-6.56046	0.89778
29	H	-4.02714	1.42018	-0.58553	75	H	-4.12167	-6.74628	1.84304
30	H	-5.58446	3.30212	-0.37466	76	H	9.96182	2.26806	-0.02963
31	H	-9.90899	2.19872	-0.53942	77	O	9.58278	1.38307	-0.05547
32	H	11.47380	4.08568	-0.31250	78	C	10.12255	0.61805	1.02948
33	H	10.70189	6.24577	0.64570	79	H	9.89637	1.09475	1.98944
34	H	-8.34189	6.48051	1.39082	80	H	11.21057	0.52083	0.93403
35	H	-6.78457	4.58361	1.19743	81	C	9.51011	-0.77134	1.02069
36	N	-4.66329	-1.20879	-0.19924	82	H	10.00688	-1.36581	1.79219
37	H	-5.15865	-2.08441	-0.35116	83	O	8.10309	-0.69961	1.34814
38	C	6.34550	1.03327	0.00864	84	C	7.30713	-1.20000	0.27538
39	C	5.29597	1.87360	-0.10988	85	H	6.91280	-2.18191	0.52672
40	C	3.98275	1.30419	-0.10643	86	C	9.59736	-1.51063	-0.32365
41	C	4.84794	-0.86455	0.11355	87	H	10.41572	-1.13069	-0.94039
42	C	3.08951	3.50962	-0.33745	88	C	8.22764	-1.24849	-0.94878

43	C	4.38420	4.04529	-0.33840	89	H	8.23794	-0.28338	-1.45668
44	C	4.58758	5.41100	-0.45829	90	H	7.92911	-2.02070	-1.65807
45	H	5.60199	5.79073	-0.45495	91	O	9.79854	-2.89922	-0.02448
46	C	3.48832	6.26414	-0.57995	92	H	9.82674	-3.38916	-0.85446

dtC^{O}:^{ABP}dG (S_1)

		X	Y	Z			X	Y	Z
1	C	-1.25604	-0.79259	-0.02316	47	C	2.18620	5.88309	-0.01984
2	C	-1.26744	-2.21403	-0.09824	48	C	1.95128	4.52315	-0.22407
3	C	0.96078	-2.37873	-0.13642	49	H	7.28365	1.41562	0.01924
4	C	0.02525	-0.12190	-0.01203	50	H	1.90519	1.88646	-0.35361
5	C	-3.31003	-1.36711	-0.01785	51	H	3.68190	7.42066	0.22298
6	H	2.07248	-0.59229	-0.11062	52	H	1.34550	6.56050	0.07609
7	O	0.20072	1.09382	0.04025	53	H	0.93731	4.14318	-0.28773
8	N	-2.49593	-0.29108	0.02849	54	N	6.00570	-0.30151	-0.09206
9	N	-2.59914	-2.56512	-0.08546	55	N	3.66078	0.06135	-0.21167
10	N	-0.23491	-3.02078	-0.14809	56	N	2.81975	2.26380	-0.58930
11	N	1.09105	-1.01575	-0.07634	57	O	4.51002	-2.03190	0.05729
12	N	2.06435	-3.10424	-0.18435	58	O	5.43065	3.29908	-0.43625
13	H	3.02278	-2.67790	-0.11121	59	H	-7.45183	-3.05266	-0.02085
14	H	1.95256	-4.10688	-0.21830	60	O	-6.56033	-3.41458	0.03705
15	C	-7.12514	2.10521	0.11056	61	C	-6.42244	-4.48441	-0.91430
16	C	-7.43307	0.94312	0.83468	62	H	-6.55235	-4.10715	-1.93315
17	C	-6.59847	-0.16622	0.79867	63	H	-7.16489	-5.26577	-0.72435
18	C	-5.43112	-0.13694	0.03057	64	C	-5.03390	-5.06955	-0.76633
19	C	-5.11145	1.00387	-0.70913	65	H	-4.93071	-5.91359	-1.45289
20	C	-5.95139	2.10939	-0.65945	66	O	-4.06329	-4.05406	-1.12700
21	C	-8.01438	3.29168	0.15422	67	C	-3.09028	-3.93790	-0.09725
22	C	-9.41039	3.14477	0.16941	68	H	-2.21680	-4.55571	-0.31686
23	C	10.24475	4.25967	0.21133	69	C	-4.67309	-5.53178	0.66033
24	C	-9.70040	5.54416	0.23994	70	H	-5.56597	-5.67352	1.27325
25	C	-8.31433	5.70411	0.22574	71	C	-3.78553	-4.40019	1.18462
26	C	-7.47974	4.58942	0.18256	72	H	-4.40171	-3.60311	1.60285
27	H	-8.31920	0.91334	1.45694	73	H	-3.07812	-4.73387	1.94318
28	H	-6.83366	-1.04516	1.38659	74	O	-3.95153	-6.76170	0.52869
29	H	-4.22452	1.02039	-1.32602	75	H	-3.73198	-7.08406	1.41068
30	H	-5.70367	2.97925	-1.25578	76	H	10.04024	2.08620	0.57901
31	H	-9.84669	2.15340	0.12609	77	O	9.63350	1.24587	0.34378
32	H	11.32053	4.12494	0.21385	78	C	9.96343	0.28175	1.35085
33	H	10.34960	6.41160	0.27310	79	H	9.64438	0.62918	2.33993
34	H	-7.88135	6.69762	0.25595	80	H	11.04587	0.10298	1.37572
35	H	-6.40459	4.72721	0.19333	81	C	9.26327	-1.03387	1.05165
36	N	-4.63917	-1.31716	-0.00373	82	H	9.64939	-1.78250	1.75115

37	H	-5.17789	-2.19169	-0.02546	83	O	7.84450	-0.90861	1.25199
38	C	6.27034	1.09315	-0.14614	84	C	7.12369	-1.20195	0.02934
39	C	5.19583	1.92737	-0.31125	85	H	6.71323	-2.20644	0.09140
40	C	3.91129	1.41293	-0.36749	86	C	9.45686	-1.54542	-0.38592
41	C	4.68902	-0.78646	-0.07479	87	H	10.35548	-1.12556	-0.84557
42	C	3.01550	3.62470	-0.35710	88	C	8.17524	-1.09903	-1.08292
43	C	4.32950	4.12552	-0.26789	89	H	8.27993	-0.06589	-1.41499
44	C	4.56368	5.47667	-0.05741	90	H	7.92226	-1.72490	-1.94021
45	H	5.58976	5.82034	0.00558	91	O	9.56372	-2.97776	-0.31140
46	C	3.49191	6.36619	0.06327	92	H	9.62491	-3.32309	-1.20944

dtC^{O}:dG (S_0)

		X	Y	Z			X	Y	Z
1	C	-3.19949	0.99937	0.09301	36	H	-9.08401	2.02025	-0.32609
2	C	-3.74933	-0.28478	0.09892	37	O	-8.63255	1.19233	-0.13120
3	C	-1.78667	-1.34267	0.09397	38	C	-9.04520	0.20948	-1.08793
4	C	-1.78335	1.12381	0.09192	39	H	-8.80803	0.53583	-2.10652
5	C	-5.31668	1.27814	0.09515	40	H	10.12525	0.03026	-1.02042
6	H	-0.11157	-0.10502	0.08961	41	C	-8.32292	-1.10018	-0.82029
7	O	-1.10414	2.16785	0.09073	42	H	-8.73541	-1.85651	-1.49347
8	N	-4.20009	1.95957	0.08689	43	O	-6.91253	-0.97114	-1.10982
9	N	-5.11096	-0.09433	0.10890	44	C	-6.13274	-1.12780	0.07682
10	N	-3.10715	-1.46660	0.10052	45	H	-5.59763	-2.07818	0.04077
11	N	-1.14783	-0.12382	0.09219	46	C	-8.41097	-1.60205	0.62755
12	N	-1.00324	-2.43648	0.08897	47	H	-9.30277	-1.22290	1.13322
13	H	0.01908	-2.38306	0.08507	48	C	-7.11980	-1.07257	1.24889
14	H	-1.45582	-3.33585	0.09252	49	H	-7.26709	-0.04172	1.57018
15	C	4.51589	0.06413	-0.01137	50	H	-6.78191	-1.66673	2.09823
16	C	3.82636	1.22456	-0.00872	51	O	-8.43701	-3.03572	0.57298
17	C	2.39787	1.15049	0.03798	52	H	-8.44330	-3.37521	1.47546
18	C	2.45044	-1.19350	0.05839	53	H	8.32936	-0.04968	-0.27435
19	C	2.33238	3.54097	0.01550	54	O	7.65712	-0.73815	-0.31399
20	C	3.73191	3.58902	-0.02875	55	C	7.94694	-1.72441	0.68445
21	C	4.40000	4.80292	-0.05970	56	H	7.95457	-1.27379	1.68286
22	H	5.48264	4.80308	-0.09312	57	H	8.92350	-2.18839	0.50173
23	C	3.66912	5.99314	-0.04743	58	C	6.88286	-2.80696	0.64762
24	C	2.27658	5.95671	-0.00429	59	H	7.17552	-3.59418	1.34752
25	C	1.60873	4.73235	0.02731	60	O	5.61049	-2.27300	1.08239
26	H	5.59771	0.02107	-0.03171	61	C	4.63644	-2.37906	0.04623
27	H	0.65663	2.24396	0.07284	62	H	3.93279	-3.17693	0.27232
28	H	4.19241	6.94113	-0.07175	63	C	6.63349	-3.42588	-0.73663
29	H	1.70535	6.87691	0.00525	64	H	7.50135	-3.31318	-1.39127
30	H	0.52621	4.68856	0.06129	65	C	5.41731	-2.65188	-1.24357
31	N	3.84768	-1.13920	0.02453	66	H	5.74458	-1.71462	-1.69523
32	N	1.76475	-0.01412	0.07185	67	H	4.82913	-3.21168	-1.97099

33	N	1.68995	2.29422	0.04840	68	O	6.34140	-4.81455	-0.52571
34	O	1.86289	-2.28645	0.06886	69	H	6.14594	-5.21870	-1.37899
35	O	4.49278	2.43265	-0.04344	70	H	-6.31859	1.68023	0.07233

dtC^{O}:dG (S_1)

		X	Y	Z			X	Y	Z
1	C	3.19655	1.00944	-0.10587	36	H	9.08045	2.00748	0.37694
2	C	3.74232	-0.27645	-0.11756	37	O	8.62809	1.18260	0.17155
3	C	1.77455	-1.32505	-0.13506	38	C	9.02651	0.19181	1.12618
4	C	1.78085	1.13726	-0.11301	39	H	8.77863	0.51194	2.14419
5	C	5.31476	1.28129	-0.08968	40	H	10.10670	0.00957	1.06986
6	H	0.09612	-0.08539	-0.13034	41	C	8.30321	-1.11368	0.84120
7	O	1.10821	2.18747	-0.10689	42	H	8.70610	-1.87610	1.51332
8	N	4.20021	1.96634	-0.08461	43	O	6.89016	-0.98262	1.11611
9	N	5.10499	-0.09031	-0.11577	44	C	6.12296	-1.12715	-0.08051
10	N	3.09560	-1.45503	-0.13304	45	H	5.58445	-2.07603	-0.05775
11	N	1.13925	-0.10497	-0.12813	46	C	8.40564	-1.60522	-0.60924
12	N	0.98868	-2.41722	-0.14576	47	H	9.30442	-1.22570	-1.10211
13	H	-0.03558	-2.36567	-0.14339	48	C	7.12341	-1.06631	-1.24090
14	H	1.44160	-3.31649	-0.14792	49	H	7.27796	-0.03352	-1.55240
15	C	-4.53331	0.06732	0.01680	50	H	6.79310	-1.65263	-2.09862
16	C	-3.79126	1.22299	-0.00043	51	O	8.42579	-3.03934	-0.56488
17	C	-2.39742	1.16002	-0.06630	52	H	8.44053	-3.37235	-1.46966
18	C	-2.40883	-1.17538	-0.09469	53	H	-8.35812	-0.08488	0.21638
19	C	-2.29211	3.53624	-0.01782	54	O	-7.67573	-0.76138	0.28041
20	C	-3.73479	3.56556	0.03036	55	C	-7.93929	-1.77539	-0.69744
21	C	-4.43095	4.77178	0.07549	56	H	-7.94256	-1.34843	-1.70633
22	H	-5.51279	4.74279	0.11136	57	H	-8.91140	-2.24869	-0.51399
23	C	-3.73150	5.96617	0.07354	58	C	-6.86081	-2.84260	-0.62538
24	C	-2.31359	5.95659	0.02833	59	H	-7.14293	-3.65262	-1.30394
25	C	-1.60668	4.77632	-0.01569	60	O	-5.59355	-2.30888	-1.06746
26	H	-5.61453	0.04165	0.03423	61	C	-4.61920	-2.36705	-0.01695
27	H	-0.62200	2.29448	-0.08676	62	H	-3.90868	-3.16605	-0.21297
28	H	-4.26552	6.90685	0.10707	63	C	-6.61486	-3.42032	0.77715
29	H	-1.77667	6.89737	0.02831	64	H	-7.49030	-3.30324	1.42141
30	H	-0.52412	4.76856	-0.05008	65	C	-5.41438	-2.61663	1.27288
31	N	-3.85062	-1.12701	-0.02324	66	H	-5.75670	-1.67145	1.69598
32	N	-1.72507	-0.02772	-0.11407	67	H	-4.82533	-3.14988	2.01958
33	N	-1.65838	2.35044	-0.06365	68	O	-6.30234	-4.81072	0.60669
34	O	-1.86927	-2.29777	-0.12700	69	H	-6.09875	-5.18582	1.47123
35	O	-4.46322	2.41860	0.03994	70	H	6.31767	1.68011	-0.05578

Fig. S11. FMOs involved in the absorption and emission processes of dtC^{O} (upper panel), dtC^{O}:^{ABP}dG (middle panel), dtC^{O}:dG (lower panel).

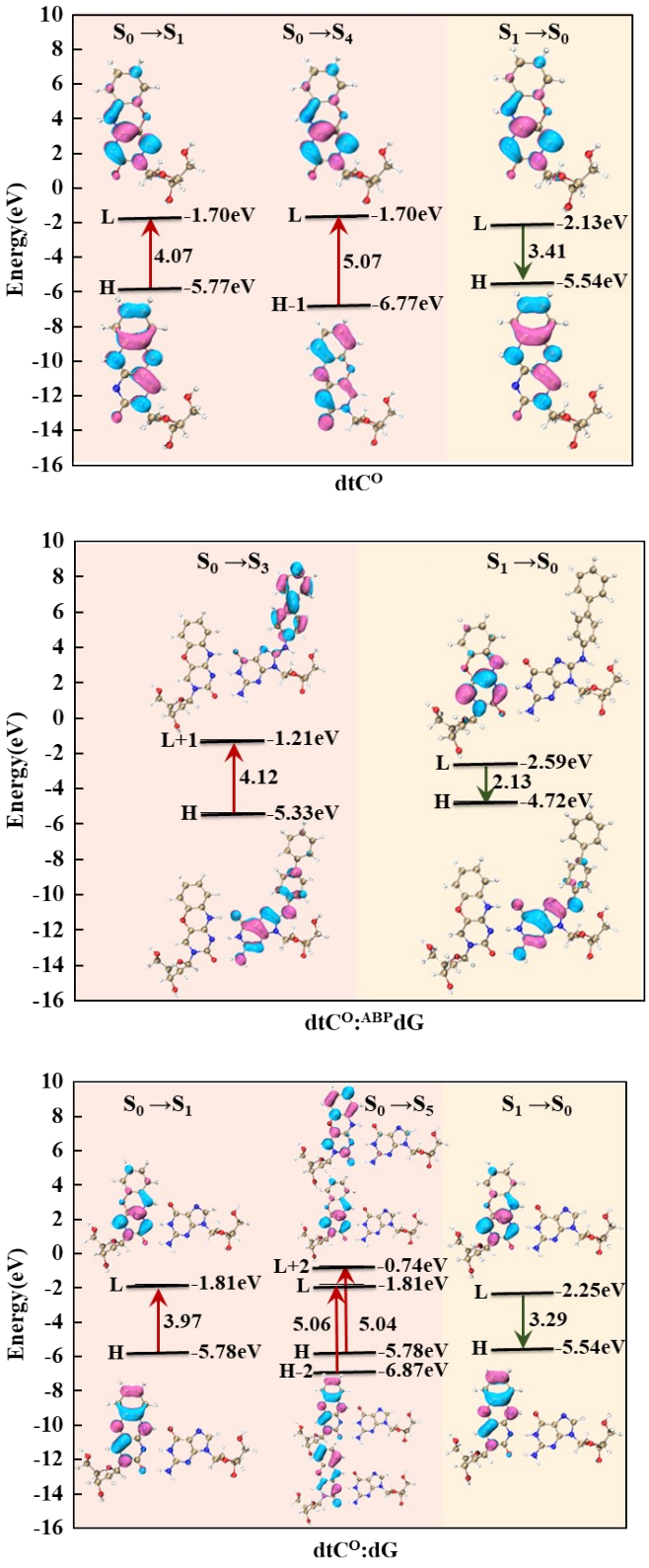


Table S8. Absorption/fluorescence wavelengths (λ), corresponding oscillator strengths ($f_{abs.}$ and $f_{flu.}$), and state assignments for dtC^O, dtC^O:^{ABP}dG, dtC^O:dG.

Optical spectral	Monomer/ Base pair	Transition	λ(nm)	$f_{abs.}/f_{flu.}$	Assignment(CI/Type/Gap(eV))
Absorption	dtC^O	$S_0 \rightarrow S_1$	358	0.20	H→L(97.2%/ππ*/4.07)
		$S_0 \rightarrow S_4$	271	0.34	H-1→L(70.7%/ππ*/5.07)
	dtC^O:^{ABP}dG	$S_0 \rightarrow S_3$	340	0.71	H→L+1(98.1%/ππ*/4.12)
	dtC^O:dG	$S_0 \rightarrow S_1$	366	0.21	H→L(96.9%/ππ*/3.97)
		$S_0 \rightarrow S_5$	290	0.04	H→L+2(19.6%/ππ*/5.04)
					H-2→L(63.2%/ππ*/5.06)
Fluorescence	dtC^O	$S_1 \rightarrow S_0$	449	0.29	L→H(98.9%/ππ*/3.41)
	dtC^O:^{ABP}dG	$S_1 \rightarrow S_0$	726	0	L→H(99.8%/ππ*/2.13)
	dtC^O:dG	$S_1 \rightarrow S_0$	464	0.32	L→H(99.0%/ππ*/3.29)