211. Characterization of the Excited State Properties of Some New Photosensitizers of the Ruthenium (Polypyridine) Family

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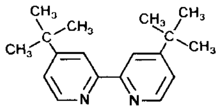
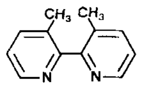
Summary

The photophysical and electron transfer properties of the lowest excited state of nine ruthenium (polypyridine) complexes have been characterized. The complexes studied are $Ru(bpy)_{3-n}(LL)_n^{2+}$, where n varies from 0 to 3, and LL is 4,4'-di-*t*-butyl-2,2'-bipyridine (DTB-bpy), 3,3'-dimethyl-2,2'-bipyridine (DM-bpy), or a 2,2'-diquinolyl derivative (DMCH). The results obtained show that the $Ru(bpy)_2(DMCH)^{2+}$ complex is expected to be a more efficient mediator than $Ru(bpy)_3^{2+}$ in the water-splitting reaction by solar energy.

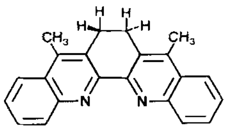
Introduction. - The search for new photosensitizers to be used in solar energy conversion processes¹) is currently very active²). Tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) is the most commonly used mediator in the photoreduction of water because it exhibits very favorable photochemical and photophysical properties. We report here the photochemical and photophysical characterization of other members of the ruthenium (polypyridine) family. The complexes studied are $Ru(bpy)_{3-n}(DTB\text{-}bpy)_n^{2+}$, $Ru(bpy)_{3-n}(DM\text{-}bpy)_n^{2+}$ and $Ru(bpy)_{3-n}(DMCH)_n^{2+}$, where n varies from 0 to 3 and the DTB-bpy, DM-bpy and DMCH ligands are as follows:



DTB-bpy



DM-bpy



DMCH

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¹) For recent reviews s. [1].

²) Among the most recent reviews s. [2].

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The syntheses, absorption spectra, ground state oxidation and reduction potentials as well as other ground state properties of these complexes are reported elsewhere [3]. The results obtained show that some of the complexes examined (particularly $Ru(bpy)_2(DMCH)^{2+}$) are expected to be more efficient mediators than $Ru(bpy)_3^{2+}$ in the water-splitting reaction by solar energy.

Experimental Part. - *Materials.* The preparation (as PF_6^- salts) and purification of the complexes is given elsewhere [3]. Triply distilled water and solvents of the best commercial grade available were used.

Apparatus. The absorption spectra were recorded with a *Perkin-Elmer* 323 spectrophotometer. The (uncorrected) emission spectra were obtained with a *Perkin-Elmer* MPF3 spectrofluorimeter equipped with a R 928 tube; excitation was carried out in the highest intensity absorption band of the visible region. Emission-lifetime measurements were carried out with a modified *Applied Photophysics* apparatus based on the single-photon counting technique; the emission decay was monitored at the maxima of the respective emission bands. Low-temperature spectra were measured by using the low-temperature accessory of the *Perkin-Elmer* spectrofluorimeter.

Procedure. The experiments were carried out on freshly prepared solutions. The complex concentration was of the order of 10^{-4}-10^{-5} M. Unless otherwise noted, the samples were degassed by repeated freeze-pump-thaw cycles. For fluid solution experiments the usual solvent was acetonitrile (some measurements, however, have also been done in water). The low-temperature (77 K) spectra were obtained using a methanol/ethanol 4:1 (*v/v*) mixed solvent which yields transparent rigid glasses.

Results. - Some of the results obtained are summarized in *Table 1* which shows the wavelengths of the absorption maxima (and the correspondent extinction coefficients) in the visible region at 293 K, the wavelengths of the emission maxima at 77 K and 293 K, and the emission lifetimes at 293 K. The emission spectra of $Ru(bpy)_3^{2+}$, $Ru(bpy)_2(DTB\text{-}bpy)^{2+}$, $Ru(bpy)_2(DM\text{-}bpy)^{2+}$ and $Ru(bpy)_2(DMCH)^{2+}$ at 293 K are displayed in *Figure 1* and those of $Ru(bpy)_3^{2+}$, $Ru(bpy)_2(DMCH)^{2+}$, $Ru(bpy)(DMCH)_2^{2+}$ and $Ru(DMCH)_3^{2+}$ at 77 K are displayed in *Figure 2*. The emission intensities of the various complexes were roughly comparable at 77 K, whereas at room temperature the emission intensity of $Ru(DMCH)_3^{2+}$ was more than two orders of magnitude lower than that of the other complexes. The emission lifetime of $Ru(DMCH)_3^{2+}$ at 77 K was 2.0 µs, not much shorter than that (5.2 µs) [4] previously found for $Ru(bpy)_3^{2+}$.

The emission lifetime of $Ru(bpy)_2(DMCH)^{2+}$ in aerated aqueous solution was 0.14 µs, to be compared with the value of 0.40 µs found for $Ru(bpy)_3^{2+}$ under the same experimental conditions. Linear *Stern-Volmer* (SV) plots were obtained for the quenching of $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_2(DMCH)^{2+}$ by methylviologen (MV^{2+}), yielding *SV*-quenching constants of $758\,M^{-1}$ and $134\,M^{-1}$, respectively (aqueous solution, room temperature, 0.5 M ionic strength). The corresponding bimolecular quenching constants are $1.89 \times 10^9\,M^{-1}\,s^{-1}$ and $0.96 \times 10^9\,M^{-1}\,s^{-1}$.

Discussion. - *Emission spectra.* The results obtained show that the emission spectra of the complexes containing DTB-bpy and DM-bpy as ligands *(Table 1, Fig. 1)* are very similar to one another and also to that of the parent $Ru(bpy)_3^{2+}$ complex, as was found to be the case for the absorption spectra [3]. This shows that in all complexes of the $Ru(bpy)_{3-n}(DTB\text{-}bpy)_n^{2+}$ and $Ru(bpy)_{3-n}(DM\text{-}bpy)_n^{2+}$ families the emitting state has to be the lowest (formally spin-forbidden) metal-to-ligand charge transfer (MLCT) excited state which is known to be responsible for the $Ru(bpy)_3^{2+}$ emission [5]. The absorption spectra of the complexes containing

Table 1. *Spectroscopic Properties*[a])

Complex (M)	Absorption[b])	Emission		
	λ_{max} [nm (ε)]	77 K[c])	293 K	293 K
		λ_{max} [nm]	λ_{max} [nm]	τ [µs]
Ru(bpy)$_3^{2+}$	452 (13000)	582	615	1.10
Ru(bpy)$_2$(DTB-bpy)$^{2+}$	450 (14500)	590	625	1.17
Ru(bpy)(DTB-bpy)$_2^{2+}$	454 (15300)	590	630	1.07
Ru(DTB-bpy)$_3^{2+}$	456 (16800)	575	625	1.15
Ru(bpy)$_2$(DM-bpy)$^{2+}$	448 (11500)	595	620	0.74
Ru(bpy)(DM-bpy)$_2^{2+}$	453 (12240)	590	625	0.72
Ru(DM-bpy)$_3^{2+}$	456 (10830)	595	625	0.21
Ru(bpy)$_2$(DMCH)$^{2+}$	448 (8310) 528 (9410)	720	736	0.38
Ru(bpy)(DMCH)$_2^{2+}$	489 (6340) 559 (9640)	737	742	0.39
Ru(DMCH)$_3^{2+}$	496 (7560) 540 (10550)	732	~740	[d])

[a]) In acetonitrile solution, unless otherwise specified. [b]) Ref. [3]. [c]) In MeOH/EtOH 4:1 (*v/v*). [d]) Not measurable owing to the too low emission intensity.

the DMCH ligand [3] *(Table 1)* are characterized by high intensity bands, which lie at lower energies than the visible absorption band of Ru(bpy)$_3^{2+}$. As previously discussed [3], such low-energy bands are due to charge-transfer (CT.) transitions from the metal to the DMCH ligand which has a much higher electronic affinity than bpy. As expected, the emission bands of the complexes containing DMCH lie at lower energies than that of Ru(bpy)$_3^{2+}$. At 77 K the emission intensities and lifetimes of the DMCH complexes are comparable to those of Ru(bpy)$_3^{2+}$, confirming that the emitting excited state is MLCT in all cases[3]). At 77 K, the emission bands of the DMCH complexes have a rather different shape compared to that of Ru(bpy)$_3^{2+}$, and among the DMCH complexes the emission of Ru(bpy)$_2$-(DMCH)$^{2+}$ is quite broader than that of the other ones *(Fig. 2)*. At room temperature, the emission of Ru(DMCH)$_3^{2+}$ becomes much weaker than that of the other members of the Ru(bpy)$_{3-n}$(DMCH)$_n^{2+}$ family. Ru(bpy)$_2$(DMCH)$^{2+}$ may exist as two different conformers of slightly different energy[4]), and since it has been shown that the coordinated DMCH ligand is not undergoing interconversion among different conformations on an NMR. time-scale [3], it can be thought that both conformers may be present in the ground and/or excited state. The very peculiar shape of the Ru(bpy)$_2$(DMCH)$^{2+}$ emission band is indeed suggestive of two, partially overlapping, almost isoenergetic emissions involving two conformers. Conformers are also possible for Ru(bpy)(DMCH)$_2^{2+}$ and Ru(DMCH)$_3^{2+}$, but for these complexes they are presumably much more different in energy (due to the increased steric hindrance brought about by the additional DMCH ligands) and

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[3]) The reason for the low emission intensity of Ru(DMCH)$_3^{2+}$ at high temperature will be discussed later on.

[4]) These conformers [6] are *Δ(δ)* and *Δ(λ)*, or their enantiomers *Λ(λ)*, *Λ(δ)*.

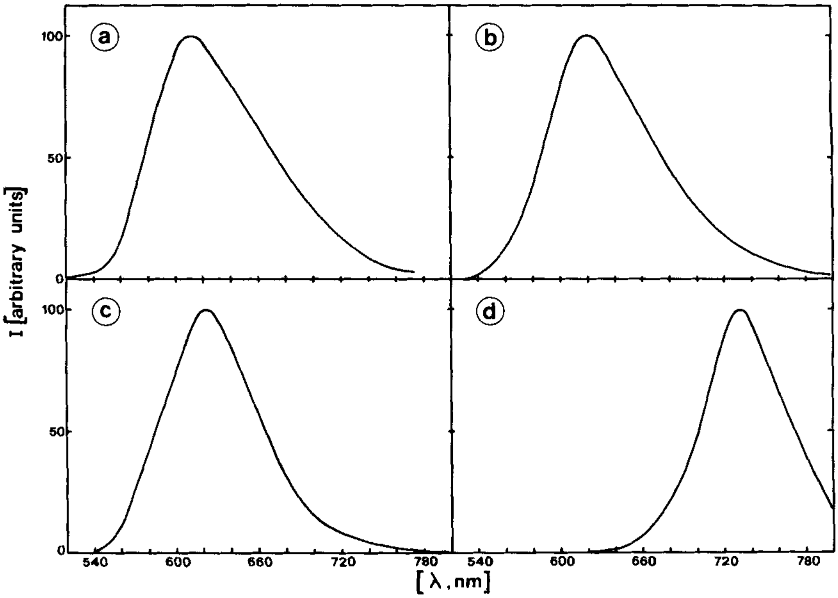

Fig. 1. *Emission spectra of* $Ru(bpy)_3^{2+}$ *(a),* $Ru(bpy)_2(DTB\text{-}bpy)^{2+}$ *(b),* $Ru(bpy)_2(DM\text{-}bpy)^{2+}$ *(c) and* $Ru(bpy)_2(DMCH)^{2+}$ *(d) at 293 K*

thus emission can be expected to occur only from that at lowest energy. We would also like to note that the emission bands of the complexes containing DMCH (with the possible exception of $Ru(bpy)_2(DMCH)^{2+}$ if the interpretation based on conformer emissions is not valid) are rather narrow and devoided of vibrational structure, indicating that emission originates from a very delocalized excited state of a quite rigid molecular structure. Finally, it may be interesting to note that in the $Ru(bpy)_{3-n}(DMCH)_n^{2+}$ family the energies of the emission bands and of the lowest absorption bands exhibit the same trend, decreasing with increasing n from 0 to 2 and then decreasing for n = 3.

Emission lifetimes. The lifetime obtained for $Ru(bpy)_3^{2+}$ in acetonitrile solution *(Table 1)* is somewhat longer than that previously reported (0.85 µs) by *Young et al.* [7] in acetonitrile solution containing 0.1 M $N(butyl)_4ClO_4$, which was probably obtained in aerated solution.

As already known from other studies [8], the excited-state lifetime depends sensitively upon the ligand nature. While *t*-butyl substitution in the 4,4′ positions only causes very minor changes, methyl substitution in the sterically hindered 3,3′ positions causes a considerable decrease in the excited-state lifetime *(Table 1)*. Since the main deactivation channel of the emitting excited state of $Ru(bpy)_3^{2+}$ at room temperature is an activated radiationless transition to a higher metal centered excited state [9], the observed decrease in the excited state lifetime upon 3,3′-methyl substitution *(Table 1)* might be due to a smaller energy gap between the emitting state and the upper lying metal-centered (MC) excited state.

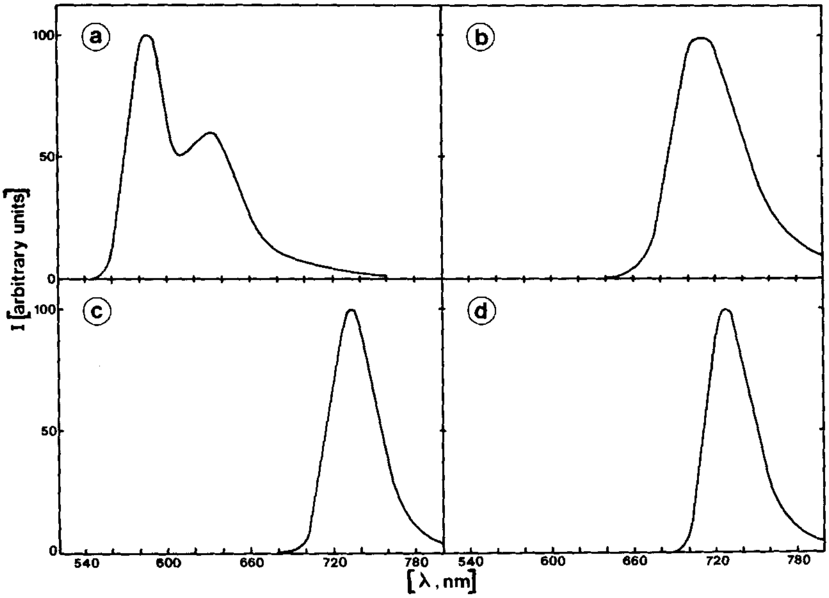

Fig. 2. *Emission spectra of* $Ru(bpy)_3^{2+}$ *(a),* $Ru(bpy)_2(DMCH)^{2+}$ *(b),* $Ru(bpy)(DMCH)_2^{2+}$ *(c) and* $Ru(DMCH)_3^{2+}$ *(d) at 77 K*

The emission lifetime also decreases replacing bpy with DMCH *(Table 1)*. For $Ru(DMCH)_3^{2+}$ the emission lifetime at room temperature could not be measured because of the too low emission intensity. At 77 K, however, the emission intensity of $Ru(DMCH)_3^{2+}$ is high and its lifetime is not much shorter than that of $Ru(bpy)_3^{2+}$. This suggests that the emission lifetime of $Ru(DMCH)_3^{2+}$ at room temperature is very short, which is consistent with the presence of an activated radiationless transition to upper MC excited states, whose energy is expected to be relatively lower in the strongly sterically hindered $Ru(DMCH)_3^{2+}$ complex. A very low ligand field strength of the DMCH ligand in the $Ru(DMCH)_3^{2+}$ complex is certainly expected on the basis of the longer Ru,N-bond distance (2.10 Å, to be compared with 2.056 Å of $Ru(bpy)_3^{2+}$) recently revealed by x-ray structural investigations [10].

Expected ability as photosensitizers. Electron transfer photosensitizers to be used in solar energy conversion systems have to satisfy several requirements. Some of these are directly related to the properties listed in *Table 2*. One can see that the DTB-bpy and DM-bpy complexes have properties quite similar to those of $Ru(bpy)_3^{2+}$. This is not the case, however, as far as the DMCH complexes are concerned. For example, the $Ru(bpy)_2(DMCH)^{2+}$ complex is able to absorb a larger fraction of solar radiation than $Ru(bpy)_3^{2+}$, if appropriate concentrations are used (*Table 1* and [3]). Also, the emission spectra show that for all the DMCH complexes the threshold energy to form the lowest excited state is much lower than for $Ru(bpy)_3^{2+}$. This is again an advantage because one could, in principle, obtain the excited state of DMCH complexes by using lower energy sensitizers. On the other hand, the lower energy content of the excited DMCH complexes as compared to $\mathrm{Ru(bpy)_3^{2+}}$ does not seem to compromise the use of these complexes as photosensitizers in the water-splitting cycle. The thermodynamic energy needed for splitting water is 1.23 eV, so that any excess energy in the excited state of the photosensitizer cannot be converted into chemical energy. For example, when $\mathrm{Ru(bpy)_3^{2+}}$ is used as a photosensitizer and methylviologen ($\mathrm{MV^{2+}}$) as an electron relay in the water splitting cycle (equations 1-4), about 0.4 eV are lost in the excited state quenching reaction (equ. 2).

$$\mathrm{Ru(bpy)_3^{2+}} + h\nu \rightarrow {}^*\mathrm{Ru(bpy)_3^{2+}} \quad \Delta G = +2.12 \tag{1}$$

$$^*\mathrm{Ru(bpy)_3^{2+}} + \mathrm{MV^{2+}} \rightarrow \mathrm{Ru(bpy)_3^{3+}} + \mathrm{MV^{+}} \quad \Delta G = -0.41 \tag{2}$$

$$\mathrm{Ru(bpy)_3^{3+}} + 1/2\,\mathrm{H_2O} \rightarrow \mathrm{Ru(bpy)_3^{2+}} + \mathrm{H^+} + 1/4\,\mathrm{O_2} \quad \Delta G = -1.26 \tag{3}$$

$$\mathrm{MV^+} + \mathrm{H^+} \rightarrow \mathrm{MV^{2+}} + 1/2\,\mathrm{H_2} \quad \Delta G = -0.45 \tag{4}$$

The excited $\mathrm{Ru(bpy)_2(DMCH)^{2+}}$ complex is able to undergo reaction 2 at a sufficiently fast rate ($k_2 = 0.96 \times 10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$)5)) in spite of its much smaller excited state energy, giving rise to $\mathrm{MV^+}$ and to the one-electron oxidized ruthenium complex which has about the same reduction potential *(Table 2)* as $\mathrm{Ru(bpy)_3^{3+}}$. Thus, the oxidative (equ. 3) and reductive (equ. 4) steps of the water splitting cycle are not affected by the smaller excited state energy of the DMCH complexes, whereas the overall efficiency of energy conversion should be improved because of the larger fraction of the solar spectrum that can be used for photoexcitation. Another weak point of the $\mathrm{Ru(bpy)_3^{2+}} \cdot \mathrm{MV^{2+}}$ system is the small cage escape yield of the primary products (equ. 2). A more detailed description of reaction 2 is in fact the following:

$$\begin{tikzcd}
 & & \mathrm{Ru(bpy)_3^{2+} + MV^{2+}} & \\
{}^*\mathrm{Ru(bpy)_3^{2+} + MV^{2+}} \arrow[r, shift left, "k_d"] & {}^*\mathrm{Ru(bpy)_3^{2+} \cdot MV^{2+}} \arrow[l, shift left, "k_{-d}"] \arrow[r, shift left, "k_e"] & \mathrm{Ru(bpy)_3^{3+} \cdot MV^{+}} \arrow[l, shift left, "k_{-e}"] \arrow[u, "k_b"'] \arrow[r, shift left, "k'_{-d}"] & \mathrm{Ru(bpy)_3^{3+} + MV^{+}} \arrow[l, shift left, "k'_d"]
\end{tikzcd} \tag{5}$$

Of course only $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{MV^+}$ which escape from the solvent cage can be involved in the useful reactions 3 and 4. Unfortunately about 80% of the caged $\mathrm{Ru(bpy)_3^{3+}} \cdot \mathrm{MV^+}$ pairs undergo a back electron transfer reaction [2c] [11] where the converted energy is immediately dissipated as heat. This is not surprising since the back electron transfer reaction is expected to be very fast because of its

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5) Although both the rate constant and the excited state lifetime are smaller for $\mathrm{Ru(bpy)_2(DMCH)^{2+}}$ than for $\mathrm{Ru(bpy)_3^{2+}}$, almost complete quenching of $^*\mathrm{Ru(bpy)_2(DMCH)^{2+}}$ can be obtained with appropriate $\mathrm{MV^{2+}}$ concentrations.

Table 2. *Properties of the complexes related to their use as photosensitizers*[a])

Complex (M)	$E_{1/2}$[b]) (M^+/M) (V)	$E_{1/2}$[b]) (M/M^-) (V)	E^{00}[c]) (eV)	$\tau^{293\,K}$ (μs)	E^0 $(M^+/{}^*M)$ (V)	E^0 $({}^*M/M^-)$ (V)
$Ru(bpy)_3^{2+}$	1.26	−1.35	2.13	1.10	−0.87	0.78
$Ru(bpy)_2(DTB\text{-}bpy)^{2+}$	1.21	−1.37	2.10	1.17	−0.89	0.73
$Ru(bpy)(DTB\text{-}bpy)_2^{2+}$	1.16	−1.39	2.10	1.07	−0.94	0.71
$Ru(DTB\text{-}bpy)_3^{2+}$	1.11	−1.44	2.16	1.15	−1.05	0.72
$Ru(bpy)_2(DM\text{-}bpy)^{2+}$	1.22	−1.37	2.08	0.74	−0.86	0.71
$Ru(bpy)(DM\text{-}bpy)_2^{2+}$	1.18	−1.41	2.10	0.72	−0.92	0.69
$Ru(DM\text{-}bpy)_3^{2+}$	1.15	−1.46	2.08	0.21	−0.93	0.62
$Ru(bpy)_2(DMCH)^{2+}$	1.25	−1.00	1.72	0.38	−0.47	0.72
$Ru(bpy)(DMCH)_2^{2+}$	1.25	−0.92	1.68	0.39	−0.43	0.76
$Ru(DMCH)_3^{2+}$	1.26	−0.90	1.69	-	−0.43	0.79

[a]) All values are for acetonitrile solution. [b]) All potentials are relative to that of the $Ru(bpy)_3^{+/2+}$ couple set at + 1.26 V. [c]) Energy of the 0-0-transition of the emitting state.

exergonicity and small intrinsic barrier. Rather, as recently pointed out by *Sutin et al.* [12], it is somewhat surprising that a finite cage escape yield is obtained. The possibility that the back electron transfer reaction is relatively slow because it lies in the *Marcus* inverted region does not seem likely since such an inverted behavior is generally not observed in fluid solution [1g] [13][6]). A more likely explanation for the relatively low rate of the back electron transfer reaction could be a non-adiabatic character imposed by the relatively small overlap between the π^*-donor orbital of MV^+ and the metal-centered t_{2g} acceptor orbital of $Ru(bpy)_3^{3+}$ [12]. For the DMCH complexes it can be expected that the back electron-transfer reaction exhibits a larger non-adiabatic character than for $Ru(bpy)_3^{2+}$ because of the increasing shielding of the t_{2g} metal orbitals by the very bulky DMCH ligand[7]). This would cause a more efficient cage escape and should thus lead to a more efficient energy conversion.

Of course, other chemical and photochemical properties of the DMCH complexes should be studied and compared to those of $Ru(bpy)_3^{2+}$ before drawing definitive conclusions on their relative abilities to act as electron transfer photosensitizers in the water splitting cycle.

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[6]) A possible exception is the very small decrease in the rate constant with increasing exergonicity reported in [14].

[7]) This might also be the case for the DTB-bpy complexes.

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