BIOMIMETIC MODELS IN ARTIFICIAL PHOTOSYNTHESIS

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NATURAL photosynthesis provides one of the best known examples of light driven redox reactions using solar irradiance for the production of O_2 and fixation of CO_2. Development of molecular assemblies to accomplish direct quantum conversion processes has been one of the challenging problems. Among the various approaches available, biomimetic methods offer an important and promising pathway towards achieving artificial systems. Biomimetism implies duplication of functions performed by molecular entities in biological systems either by modifying or by isolating certain salient features pertinent to the real systems. Thus, development of biomimetic devices require a pre-knowledge of structure and organization of molecular entities and their *in vivo* mechanistic features. The advantage of the artificial devices is the 'fine tuning' possible in the flexible synthetic systems not only to accomplish the production of O_2 and fixation of CO_2 but also reduction of N_2 and production of H_2. Moreover, the model compounds provide a convenient approach to understand hitherto complex mechanistic pathways in natural photosynthesis.

The photosynthetic apparatus located in the thylakoid membrane consists of an 'antenna' for light harvesting and photosystems (PS) I and II wherein the reaction centres (RC) are located (figure 1). The pigment molecules, chlorophylls (Chl) are intimately associated with protein both in the antenna and RC complexes. The accepted dogma being that the incident light is harvested by antenna and rapidly transducted to RC within a few nano seconds[1]. In the RC, the excited state of the pigment is a strong reductant and an electron is lost to an acceptor strategically placed nearby. The charge-separation is accomplished rapidly through a series of electron acceptor-donor systems to prevent recombination losses. Some of the most intriguing problems are (i) the identification and the number of pigment molecules and their organization in the energy harvesting
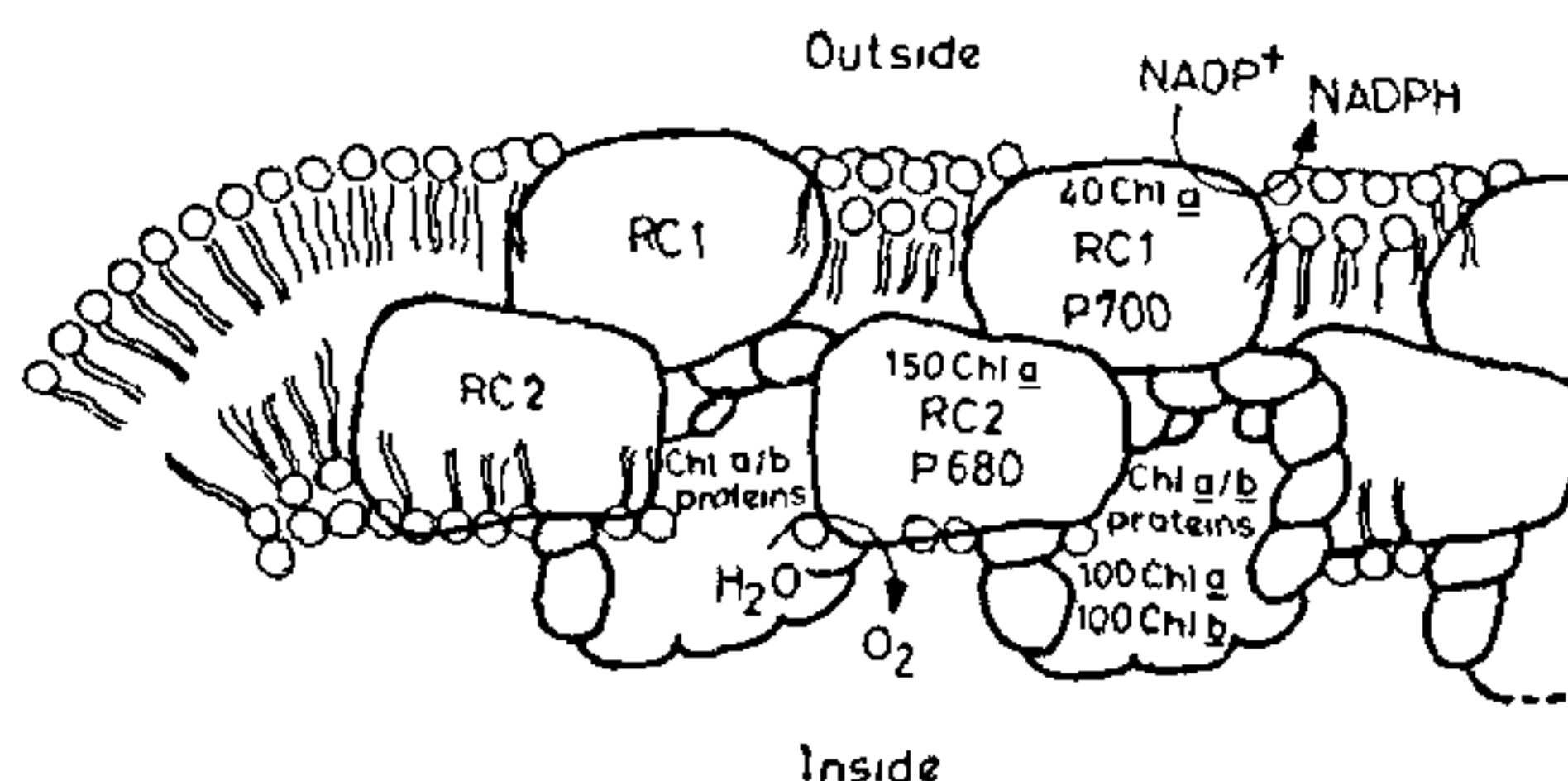

Figure 1. Thylakoid membrane depicting hypothetical positions of 'antenna' and 'reaction centre' proteins embedded in the membrane.

system, (ii) the mode of energy transport, in general, and the role of auxillary pigments both in RC and in the antenna part, (iii) identification and organization of the primary electron donor and acceptor in RC, (iv) the dynamical features of light induced electron transfer and (v) the functional role of the membrane and protein constituents. The structural features of a few chlorophylls and chlorophyll-like molecules are known[2]. They are indicative of the presence of π-π interactions forming layered structures with or without hydrogen bonding by intervening water molecules. The antenna bacteriochlorophyll (BChl)-protein structure has revealed interesting features[3]. This protein is trimeric in nature and each sub unit of the protein contains 7 BChls arranged around a 3-fold axis forming a funnel shaped array, like the disk of a radio telescope. The recent crystallization of the RC protein from *Rhodopseudomonas viridis*[4] and its EPR data revealed the orientation of the primary donor in the crystal in four magnetically nonequivalent sites[5]. Solution EPR studies on reaction centres of *Rhodospirillum rubrum* have provided a wealth of information concerning the dimeric nature of P870 cation radical[6]. It has been postulated that the primary donor-acceptor in PS of a bacterial/plant origin consists of (BChl)$_2$-bacterial pheophytin (BPheo) ligated Chl. or (Chl)$_2$-Chl re-

spectively with the estimated donor-acceptor separation around 10Å (edge to edge)[7]. The photophysical studies concerning the electron transport reveal that the rates of radical pair formation $D^+ A^-$ are in the order of $\sim 10^{11} s^{-1}$ with a recombination rate of $10^8 s^{-1}$ (scheme I).

$$k_{et} \gg (k_f + k_{IC} + k_{ISC})$$

$$k_s \gg (k_r + k_r' + k_{-et})$$
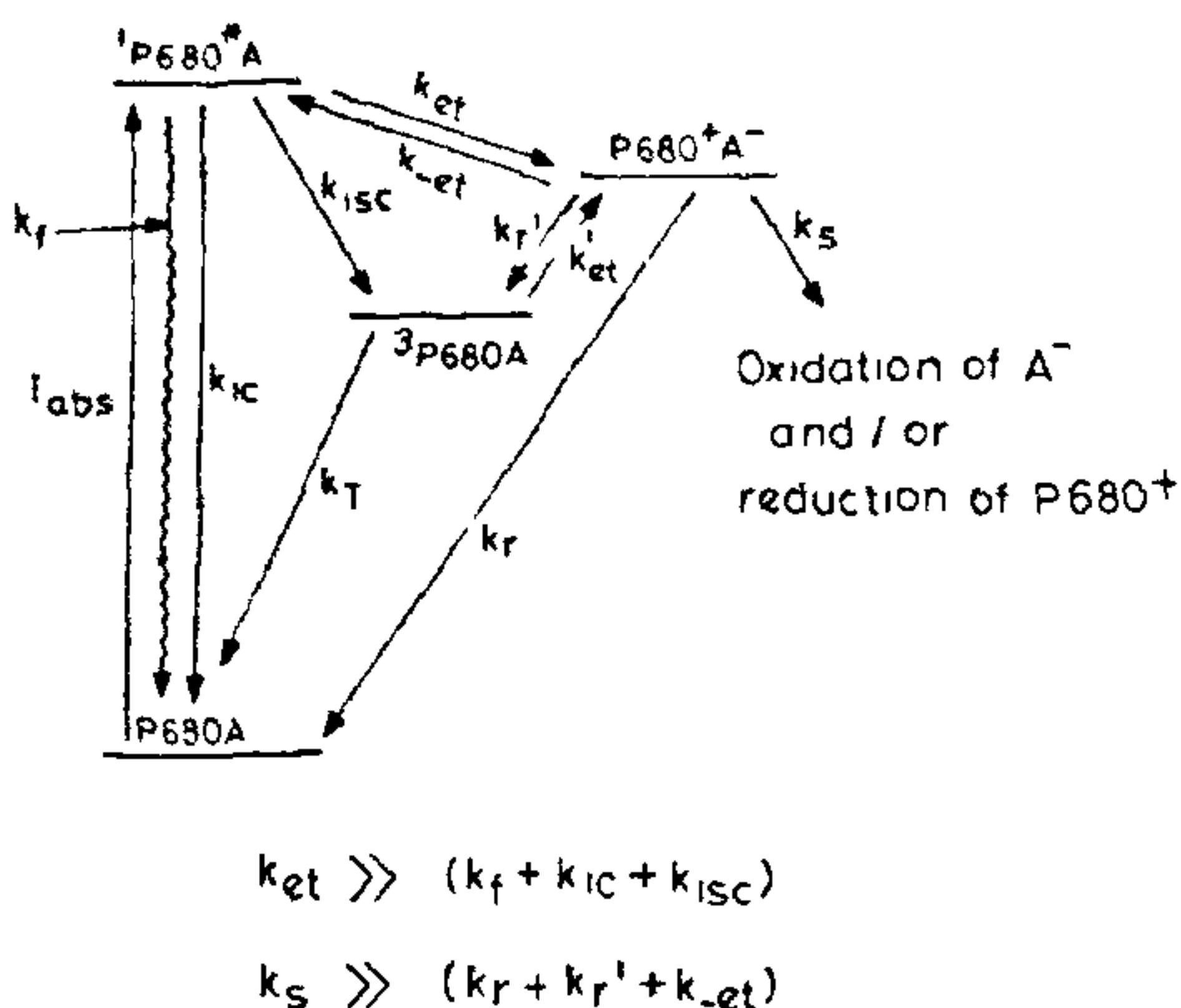
Scheme I. Possible events leading to light induced electron transfer P680 to an acceptor A. The kinetic conditions for forward electron transfer is shown.

Design of biomimetic models, would then require these in-built features to mimic photosynthetic system. Any representation of artificial system should satisfy most importantly the kinetic features (scheme 1) and stability. The model compounds involve either cell-free pigments, Ch. or completely synthetic compounds, porphyrins and other mesomolecular systems (figure 2) that bear a close resemblance to structural features of the pigment and mimic certain functions *viz.* O_2 production, rapid light-induced redox reactions, possible H_2 evolution, and adopt mechanistic pathways similar to the photosynthetic route. The assertion that the primary donor-acceptor in bacterial PS is $(BChl)_2 \cdot BPheo$. has led to the interesting formulation of synthetic dimeric, trimeric and tetrameric Chls. and porphyrins and their photophysical properties. In what follows now, we will describe the functional features of some of these systems and the level of our understanding of the real systems.

Synthetic reaction centres to mimic charge-separation have been receiving increasing atten-
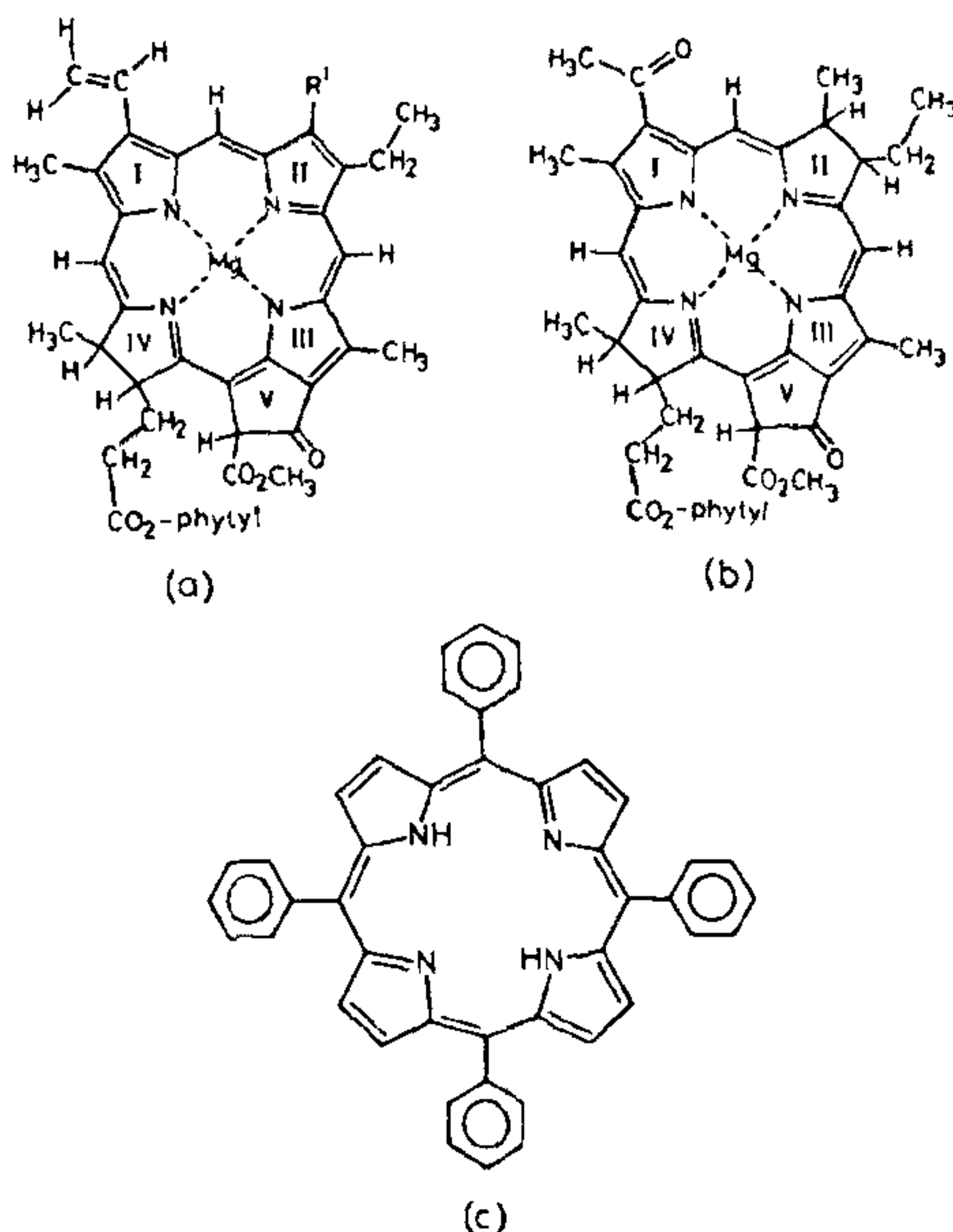
Figure 2. Molecular structures of cell-free pigments, (a) Chlorophyll *a* and (b) Bacteriochlorophyll *a*, the phytyl chain is not shown. The synthetic model compound 5, 10, 15, 20-tetraphenyl porphyrin is shown in (c)

tion[8]. The cell-free pigments, chlorophyll and its altered products, pyrochlorophyllids, pheophorbide and pheophytin (Pheo) have been employed as model compounds to investigate the photophysical properties. A tetrameric pigment where a dimeric pyro-Chl *a* is bridged to two pyroPheo *a* has been reported[9]. Interestingly, this compound resembles closely the RC complex in exhibiting a rapid forward reaction rate with a much slower recombination rate, the reaction being charge-separation between donor (PChl) dimer and PPheo *a* the acceptor. The nature of the acceptor was systematically varied to pyropheo *a* pyroChl *a* and pheo *a* in order to study their photophysical properties[10]. These studies reveal that in the model compound, $(pyroChl\ a)_2$ pheo *a*, there exists a rapid electron transfer (100 ps) accompanied by a slower transient. A few cofacial dimers involving Chl and its derivatives have

been reported[11]. None of these displays CT state, EPR and optical transients similar to that of RC complex. However, the photophysical studies of the covalently linked dimers and trimers have qualitatively improved our understanding. The life time of the excited singlet states, the free-energy change of the electron transport reaction from the excited singlet state (ΔG_{ET}) and the rates of radical-pair formation reveal that for the efficient electron transfer rate $\sim 10^{11} s^{-1}$ with a quantum yield $\sim 50\%$, the covalent bridge should consist of not more than 5 atoms. This places a restriction on the interchromophore separation at $\sim 7 Å$. In the cofacial dimers, the spatially constrained chromophore restricts the proper orientation for favourable charge-separation.

Porphyrins on the other hand from completely synthetic systems and provide structural features that are amenable for fine tuning, to understand excited energy transfers and light induced electron transfer reactions. Model studies involve covalently linked bisporphyrins[12], porphyrins endowed with side arm terminating with a functional group *viz.* quinone[13], nitrobenzene[14], carotene[15], nitrogenous bases[16] and crown ether moieties[17]. The covalently linked bisporphyrins can either be joined singly or doubly with covalent linkages. The latter bisporphyrins can assume either cofacial (plane to plane eclipsed) or displaced conformation. The advantage of using cofacial porphyrins is that the interplanar distances can systematically be varied (figure 3). Besides, the elegant synthetic procedures employed to accomplish these porphyrin systems, a study on kinetic features in picosecond time domain have yielded valuable results. Thus, the spectral studies on MgP-H$_2$P revealed that charge-separated MgP$^+$-H$_2$P$^-$ species has a life time of 500 ps and it displays a few spectral characteristics similar to PS II[18]. Moreover, the life times of the charge-separated species are shown to depend on (a) the dielectric constant of the medium *i.e.* greater polarity induces shorter life time and (b) interplanar separation *i.e.* larger separation longer life time[19]. Interestingly, in the cofacial MgP-H$_2$P dimer where the porphyrin planes are not exactly superposed, the relaxation

(a)   (b)

(c)
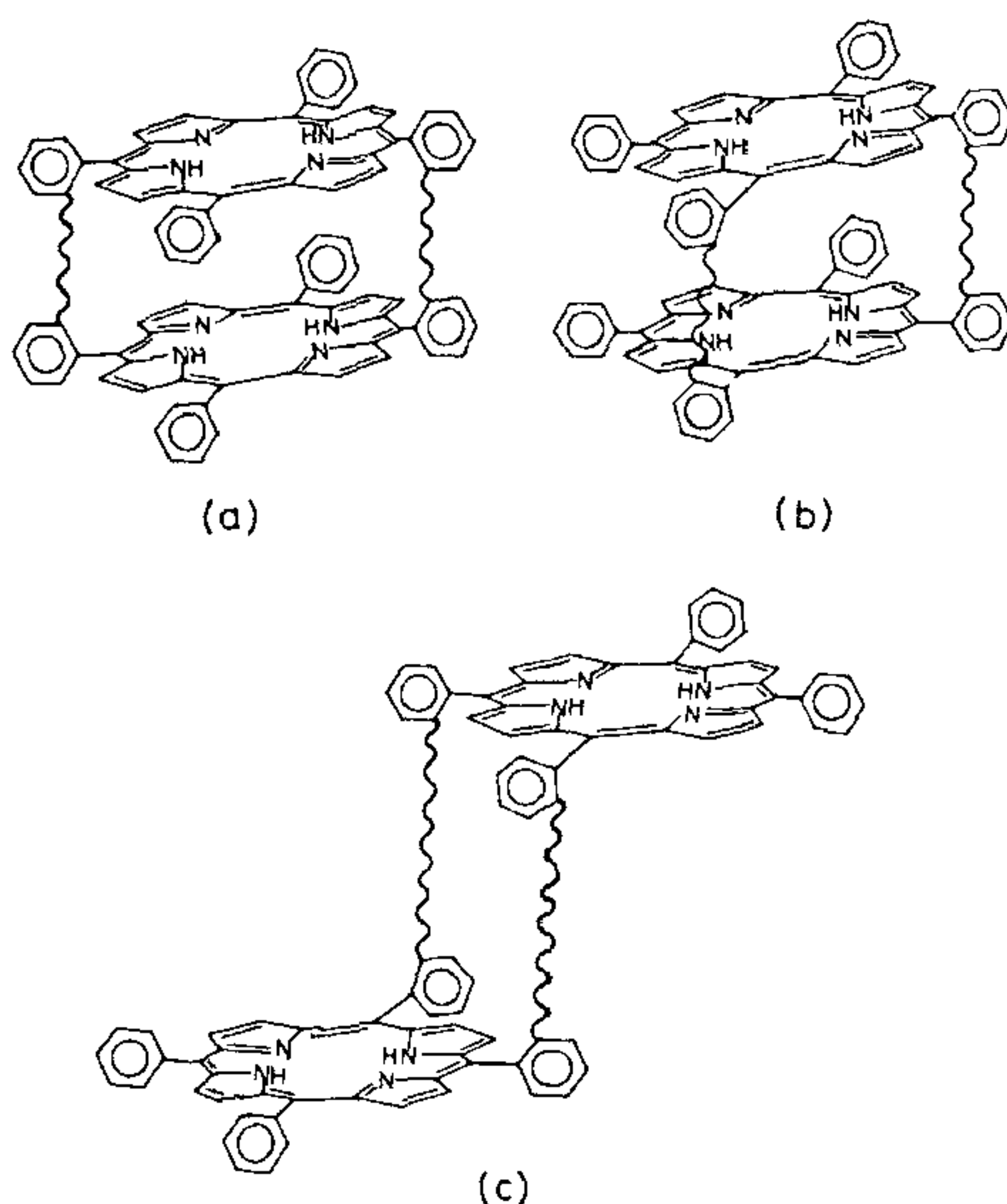
Figure 3. A representative set of biscovalently linked diporphyrin systems. The wavy line indicate the covalent linkage. The porphyrin is represented as meso-tetraphenylporphyrin.

of charge-separated species display triphasic kinetics with different life time domains reflecting the different orientations of the rings. The relevance of electron transfer to cytochrome was investigated by studying a model system, consisting of Fe(III)P and ZnP covalently linked by five atom linkage[20]. The excited state life time of Fe(III) ClP-ZnP was found to be in the order of 6ps and the charge separation Fe(III)Cl-P-ZnP $\rightarrow$ Fe(II) ClP-ZnP$^-$ occurs with a rate constant of $k \sim 10^{11} s^{-1}$. The only structural reports thus far available on the bisporphyrin system seems to be that of Collman *et al*[12] where the two porphyrin planes are displaced with an edge to edge separation of 5 Å. The models thus far known adopt either a cofacial or displaced geometries that are dictated by the nature of the covalent linkage. Bisporphyrins without a covalent linkage and having specific orientations may be nearer to the RC complex. This has been accomplished in the development of supermole-
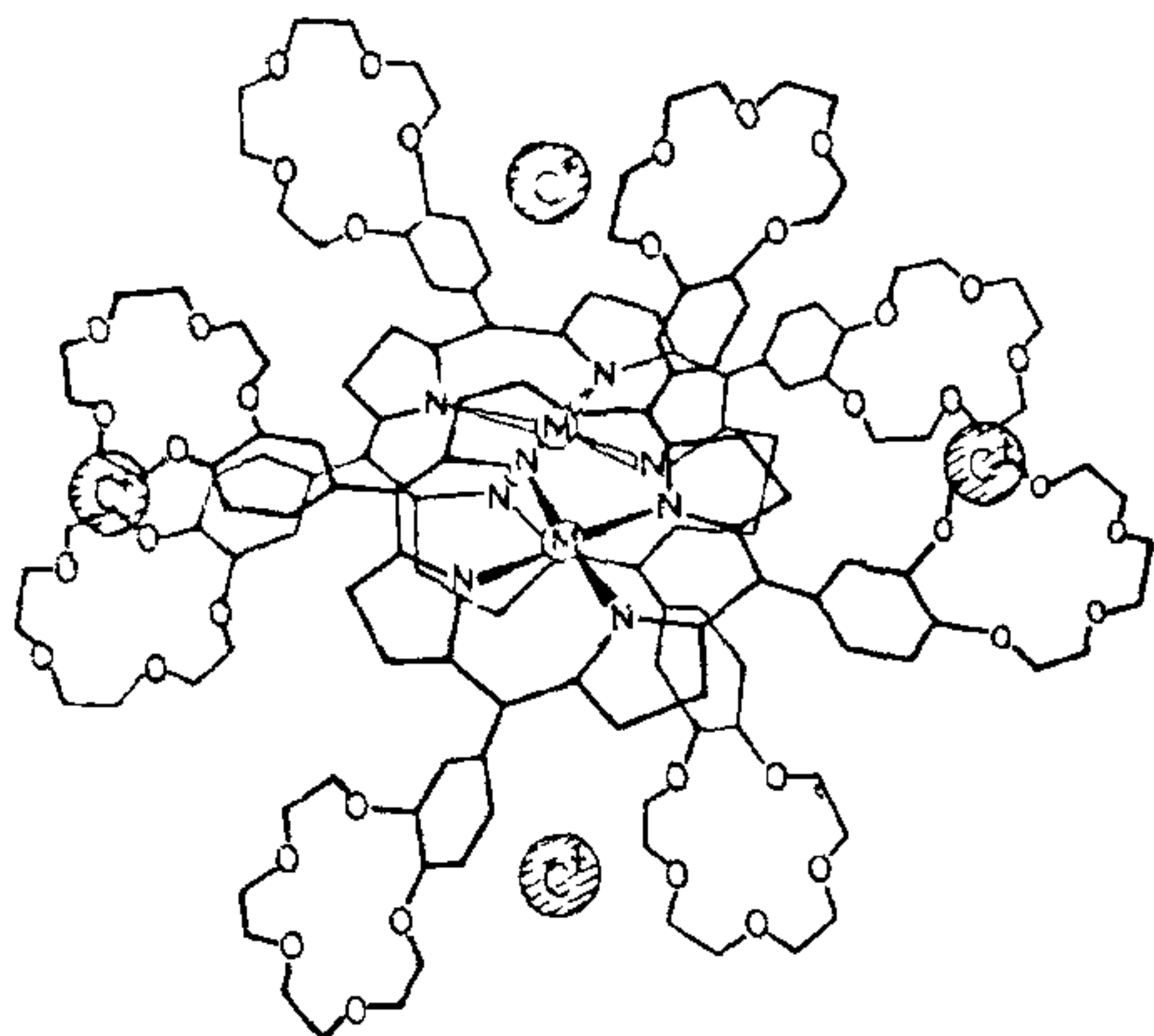
Figure 4. Supermolecular tetra(benzo-15-crown-5)-porphyrin dimer where M represents transition metal ion VO(IV), Cu(II) and Zn(II). The individual crown porphyrins are joined in a noncovalent fashion with alkali cation, C^+.

cular-entity (figure 4) where the two porphyrins bearing crown ether voids in the peripheral positions are brought together by complexation with cations with an interplanar separation of ~ 4.0 Å and the porphyrin planes are in eclipsed configuration[17]. The ring oxidation potential of Zn complex is 200 mv smaller than the ZnTPP and a rapid singlet quenching of porphyrin was observed during dimerisation[21]. Photophysical properties of the resultant triplet should provide interesting results on the orientational features. A triple-decker porphyrin containing Zn(II) ions and a free base has been reported[22]. It was shown that fluorescence life times of the trimer decreased with increasing polarity of the solvent and the measured fluorescence is proportional to the extent of quenching. Electrochemical studies revealed that CT states $ZnP_{out}^+ ZnP_{in} P^-$; ZnP_{out} $ZnP^+ P_{out}^-$ and $ZnP_{out}^+ ZnP_{in}^- P$ are at 1·83, 1·92 and 2·12 eV respectively. It is reasoned that the intermediate ZnP ensures rapid electron transfer between ZnP_{out} and P and the distance between the outermost planes is of the order of 10 Å. More interesting results are awaited in these porphyrins.

The singly linked bisporphyrins display excellent singlet-singlet energy transfers with quantum yields $\sim 80\%$[23]. These provide models for antenna part to delineate the energy transfer mechanisms in these systems. It has been shown that the porphyrin planes separated by 8 to 20 Å by different covalent linkages can be brought together by an introduction of a spacer molecule[24] leading to the formation of a folder dimer (figure 5a). The $ZnP \sim PH_2$ displays different life times (2 ns – 12 ns) and the extent of singlet quenching of the different porphyrin centres by spacer molecule proceed at different rates. These molecules provide interesting results to identify the mode of energy transfer in the antenna part and rc complex.

Porphyrins endowed with side arms bearing

(a)

(b)
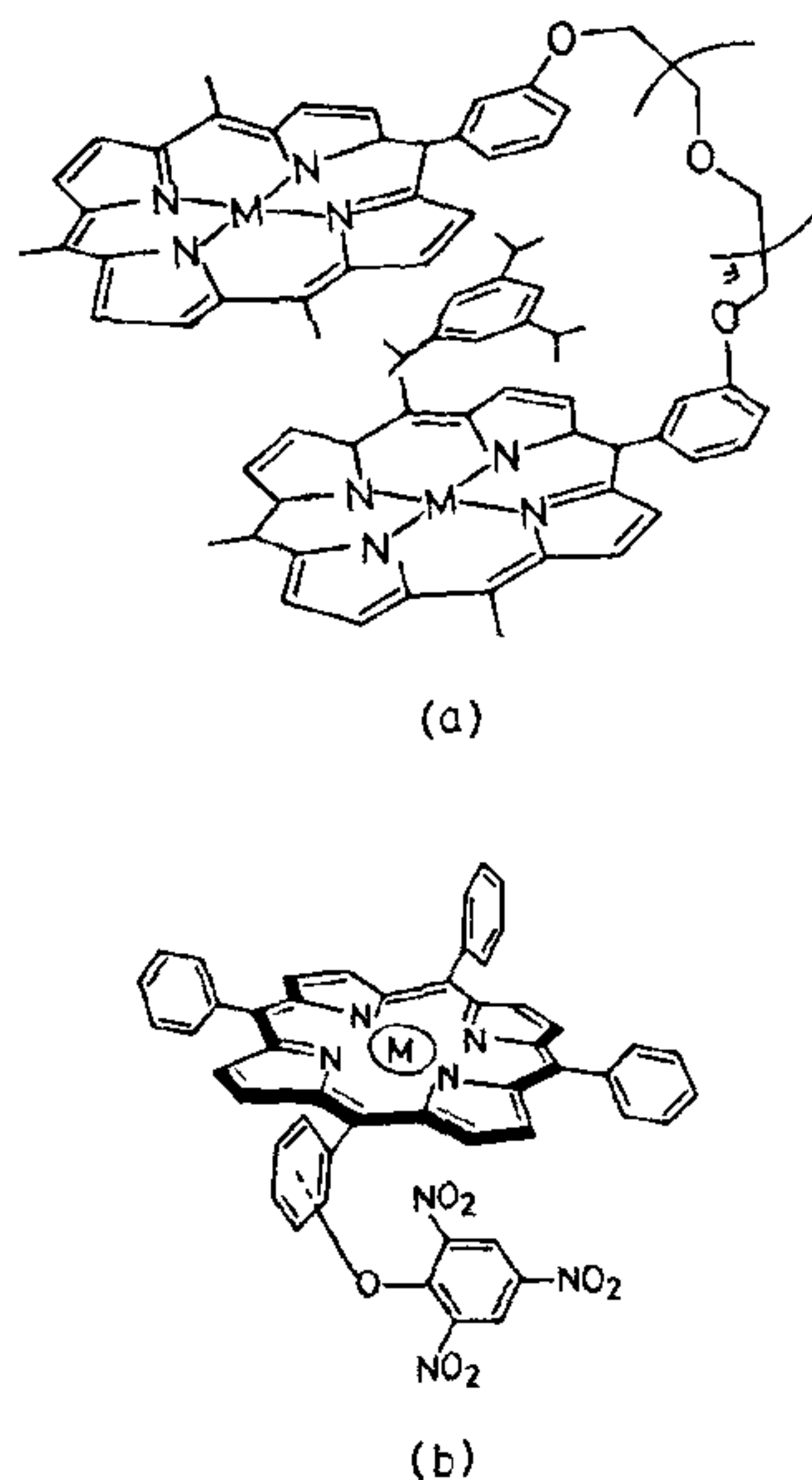
Figure 5. (a) Folded configuration of singly linked bisporphyrin dimers with varying values of n and the spacer molecule is 1,3,5-trinitrobenzene. (b) An intramolecular porphyrin(donor)-trinitrobenzene-(acceptor)-system, the latter is appended at either o, m or p positions of one of the aryl groups of the porphyrin.

quinone groups furnish models for donor-acceptor systems for the RC complex[13]. Studies on a variety of porphyrin-quinones with methylene ester groups, methylene groups of variable length, amides and porphyrins linked with mono and bisquinones, and carotenoids revealed both intramolecular CT and electron transfer reactions. The precursor for the light induced electron transfer being the singlet excited state of porphyrin. The life times of the charge-separated species are shown to increase with the increasing number of bridging atoms, $n(n = 2, \Gamma s = 70$ ps to $n = 6, \Gamma s = 2$ ns). The light induced EPR spectra of the species exhibit characteristic features attributable to $P^+ - Q^-$ and display interesting kinetic features. The assertion that the excited singlet state is the precursor comes from the flash photolysis studies and the triplet state life times. In most of the studies, quinones have been employed as acceptors and owing to their high reduction potentials, the free energy of electron transfer from excited singlet tend to be largely exergonic. In order to circumvent this, Maiya and Krishnan[14] investigated various substituted nitroaromatics appended to porphyrins at various distances (figure 5b). These porphyrins exhibit reduced singlet quantum yields, however, the redox potentials are not significantly altered compared to TPP indicating that the extent of folding of side arm over the porphyrin is minimum. Detailed studies on the life times of these species would be of interest in the elucidation of possible mechanism of energy transfers. Porphyrins endowed with bisquinones and carotenoids enclosed in BLM have been shown to exhibit enhanced photovoltages. These results are promising in that the solvent environments can indeed play a crucial role in the orientations of the chromophore.

Porphyrins, phthalocyanins and their substituted derivatives themselves display diverse photophysical properties. The metallo derivatives are often employed for the photo production of H_2 and the utility of these systems for the possible evolution has been discussed[25]. Numerous studies are avilable on nonporphyrinic ligand systems particularly of $Ru(bipy)_3^{2+}$, acridine, flavins and acridine orange as sensitizers

for H_2 production and they are classified normally under homogenous system.

CONCLUSIONS AND PROJECTIONS

The progress in biomimetic models in recent years has been substantial. The studies thus far carried out bring forth the importance of orientation of pigment molecules and acceptors. The complexity of the problems has increased since the models displaying similar spectral features as those of the real system exhibit different kinetic features. There is a wide scope to expand and persue the fundamental aspects in view of the interesting chemical, physical and biological features these system possess. Biomimetism offers more flexibility than real systems in terms of simpler structure and design of molecules in search of fuel producing since the components can be assembled as desired. Researches on hybrid systems[26] for the production of H_2 assures that the biomimetic devices approach is worthwhile in the large scale production of fuel gases and energy rich compounds. Besides, endeavours to delineate the photosynthetic functions using either cell-free or whole cell pigments have lead to a good amount of sophistication in instrumentation. Most of these studies involve ultrashort time domains. The sensitivity of probes and coupling of different techniques have been proved to be very helpful in the understanding of the nature of the excited states of the primary donor in the charge-separated species and the mechanistic pathways in the deactivation of the photo excited states. A few of the techniques that come into vogue are pulse radiolysis and photolysis, RYDMR (reaction yield detection by magnetic resonance) and ODMR (optical detection by magnetic resonance). Despite these attempts, the problems still remain elusive: (a) The roles of proteins and membranes in the organization of pigments both in the antenna part and RC have hardly been understood. Though there are a few attempts for mimicking RC, no reliable model has yet been developed for the antenna system. The orientation of the pigment molecules seem to play a dominant part as revealed by biomimetic

model studies. The positioning of the acceptor molecules in the PSs is governed by their redox states and sequencing them in proper orientation seems to be the key for proper separation. Models to investigate these aspects have yet to be designed. There seems to be a delicate balance between the rigidity and conformational mobility imposed by proteins and the model study having these in-built features have to be developed. The membrane function has been explored using vesicles and the usage of these in model system holds promise[27]. The role of auxillary pigments even in real systems has not been known with certainty[28]. These exists no models as yet for this and this is important in view of the rapid energy transfer and the role of carotenoid triplets in the energy transduction. (b) The role of manganese and proteins associated with PS II in O_2 evolution remains unclear. An interesting possibility of utilising dimeric manganese compounds seems to be attractive. (c) Several attempts have been made for the H_2 production using hybrid systems employing chloroplasts and hydrogenase and porphyrin systems[29]. These aspects have been receiving increasing attention. (d) Besides chlorophylls, there exists other photosynthetic pigments which carry out diverse roles *viz* establishing proton gradient (halobacterium) and for carrying out six electron reduction of sulphite and nitrite to H_2S and NH_3 (isobacteriochlorins or sirohemes). Thus far, no biomimetic models have been developed for this despite their important functions. A good opportunity exists to couple some of these functions to the photosynthetic system. Biomimetic approach thus involves both *in vivo* and *in vitro* experimentation. The information obtained from such studies are valuable in the design of molecular systems.

ACKNOWLEDGEMENTS

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1. Katz, J. J., In: *Chlorophyll Organization and Energy transfer in Photosynthesis CIBA Foundation Symposium* 61, Excerpta media Amsterdam 1979.
2. Barkigia, K. M., Fajer, J. and Smith, K. M., *J. Am. Chem. Soc.*, 1981, **103**, 5890 and references cited therein.
3. Mathews, B. N. and Fenna, R. I., *Acc. Chem. Res.*, 1980, **13**, 309.
4. Michel, H., *J. Molec. Biol.*, 1982, **158**, 562.
5. Gast, P., Wasielewski, M. R., Schiffer, M. and Norris, J. R., *Nature (London)*, 1983, **305**, 457.
6. Lubitz, W., Lendzian, F., Scheer, H., Gottstein, J., Plato, M. and Mobius, K., *Proc. Natl. Acad. Sci. (USA)*, 1984, **81**, 1401.
7. Davis, M. S., Forman, A. and Fajer, J., *Proc. Natl. Acad. Sci.*, 1979, **76**, 4170; Blankenship, R. E. and Parson, W. W., In: *Photosynthesis in relation to Model systems* (Ed.) J. Barber, Elsevier, Amsterdam, 1979; Holten, D., Windsor, M. W., Parson, W. W. and Gouterman, K., *Photochem. Photobiol.*, 1978, **28**, 951; Fajer, J. Davis, M. S., Forman, A., Klimov, V. V., Dolan, E. and Ke, B. J., *Am. Chem. Soc.*, 1980, **102**, 23.
8. Katz, J. J. and Hindman, J. C., In: *Photochemical Conversion and Storage of Solar Energy* (Ed.) J. S. Connolly, Academic Press, N.Y., 1981; Boxer, S. G., *Biochem. Biophys. Acta*, 1983, **726**, 625; Wasielewski, M. R., In: *Molecular Biology, Biochemistry and Biophysics*, (Ed) F. K. Kong, 1982, **35**, 234; Dolphin, D. Hion, J. Paine III, J. B., *Heterocycles*, 1981, **16**, 417.
9. Pellin, M. J., Kaufman, K. J. and Wasielewski, M. R., *Nature (London)*, 1979, **278**, 53.
10. Bucks, R. R., Netzel, J. L., Fujita, I. and Boxer, S., *J. Phys. Chem.*, 1982, **86**, 1947.
11. Wasielewski, M. R., Svec, W. A. and Cope, B. J., *J. Am. Chem. Soc.*, 1978, **100**, 1961; Bucks, R. R. and Boxer, S., *J. Am. Chem. Soc.*, 1982, **104**, 340.
12. Collman, J. R., Chong, A. O., Jameson, G. B., Oakley, R. J., Rose, E., Schmitton, E. R. and Ibers, J. A., *J. Am. Chem. Soc.*, 1981, **103**, 516; Collman, J. P., Benscome, C. S., Dwand, Jr. R. R., Kreh, R. P. and Anson, F. C., *J. Am. Chem. Soc.*, 1983, **105**, 2699; Collman, J. P., Benscome, C. S., Barnes, C. E. and Miller, B. D., *J. Am. Chem. Soc.*, 1983, **105**, 2704.
13. McIntosh, A. R., Siemiarczuk, A., Bolton, J. R., Stillman, M. J., Ho, T. F. and Weedon, A. C., *J. Am. Chem. Soc.*, 1983, **105**, 7215; Siemiarczuk, A., McIntosh, A. R., Ho, T. F., Stillman, M. R., Roach, K. J., Weedon, A. C., Bolton, J. R. and Connolly, J. S., *J. Am. Chem. Soc.*, 1983, **105**, 7224. Wasielewski, M. R. and Niemczyk, M. P., *J. Am.*

Chem. Soc., 1984, **106**, 5043; Jeyakumar, D. and Krishnan, V., (unpublished).

14. Bhaskar Maiya, G. and Krishnan, V., (unpublished), Bhaskar Maiya, G. and Krishnan, V., *Inorg. Chem. Acta.*, 1983, **77**, L-13.

15. Moore, J. A., Gust, D., Mathis, P., Mikocas, J. C. Chachaty, C., Benasson, R. V., Land, R. J., Dolizi, D., Lidell, P. A. and Lehman, W. R., *Nature (London)*, 1984, **307**, 630.

16. Suriyanarayanan, P. and Krishnan, V., *Photochem. Photobiol.*, 1983, **38**, 553.

17. Thanabal, V. and Krishnan, V., *J. Am. Chem. Soc.*, 1982, **104**, 3643; Thanabal, V. and Krishnan, V., *Inorg. Chem.* 1982, **21**, 3606.

18. Netzel, T. L., Kroger, P., Chang, C. K., Fujita, I. and Fajer, J., *Chem. Phys. Lett.*, 1979, **67**, 223; Netzel, T. L., Bergkamp, M. A. and Chang, C. K., *J. Am. Chem. Soc.*, 1982, **104**, 952.

19. Fujita, I., Fajer, J., Chang, C. K., Wang, C. B., Berkamp, M. A. and Netzel, T. L., *J. Phys. Chem.*, 1982, **86**, 3754.

20. Fujita, I., Fajer, J., Chang, C. K. and Wang, C. B. Bergkamp, M. A. and Netzel, T. L., *Proc. Natl. Acad. Sci.*, (USA), 1982, **79**, 413.

21. Bhaskar Maiya, G. and Krishnan, V., *Inorg. Chem.*, 1985.

22. Wasielewski, M. R., Niemezyk, M. P. and Svec., W. A., *Tetrahedron Lett.*, 1982, 3215.

23. Anton, J. A., Loach, P. A. and Govindjee, *Photochem. Photobiol.*, 1978, **28**, 315.

24. Jeykumar, D. and Krishnan, V., *Nouv. J. Chem.*, 1983, **7**, 697.

25. Harriman, A. and Richoux, M. C., *J. Photochem.*, 1981, **15**, 335; Harriman, A., Carnieri, N. and Porter, G., *J. Chem. Soc., Dalton)* 1982, 981; Kalyanasundaram, K. and Neumann-Spallart, M., *J. Phys. Chem.*, 1983, **86**, 5613; Harriman, A., Porter, G. and Wilowska, A., *Trans. Faraday Soc.*, 1984, **80**, 191.

26. Cuenolt, P. and Gratzel, M., *Photochem. Photobiol.*, 1982, **32**, 203; *Experentia*, 1982, **38**, 223.

27. Hurley, J. K. and Tollin, G., *Solar Energy*, 1982, **28**, 187.

28. Sauer, K., *Bioscience*, 1981, 525; Lutz, M., Chinskey, L. and Turpin, P. Y., *Photochem. Photobiol.*, 1982, **36**, 503; Koyama, M., Kito, M., Jakii, T., Saiki, K., Tankida, K. and Yamashita, *J. Biochim. Biophys. Acta*, 1982, **680**, 109.

29. Okura, I., Takenchi, M. and Kim Thuan, N., *Photochem. Photobiol.*, 1981, **33**, 413.

ANNOUNCEMENT

STRENGTH AND STRUCTURE IN CARBONS AND GRAPHITES

The Carbon Group of The Institute of Physics and The Royal Society of Chemistry is organizing a conference on Strength and Structure in Carbons and Graphites to be held at the University of Liverpool from 16–18 September 1985. The conference follows the successful meeting of the same title held at Bath in 1979. It will provide a forum for the presentation and assessment of recent advances in all aspects of the science and applications of strength and structure of carbons, cokes and graphites. Topics to be covered will include:–

1. Structure-property relationships, 2. Fracture behaviour, 3. Fibres, composites and multiphase materials, 4. Biomedical applications.

Reviews will be presented by the following invited speakers.

1. 'Effects of weak interfaces on the thermal expansion and mechanical behaviour of carbon-carbon composites' J Jortner (Jortner Research and Engineering Inc., California), 2. 'Carbon composites: their use and potential for non-aerospace applications' A Sherrin (Dunlop Technology Division, Birmingham), 3. 'Relation between raw material (pitch and coke) and mechanical properties of products' H Tillmans (Sigri Electrographit GMBH, Frankfurt), 4. 'The fracture of polycrystalline graphites' M Tucker (CEGB Berkeley Nuclear Laboratories, Glos).

A call for papers, further information and registration details will be available in May 1985, from the Meetings Officer, The Institute of Physics, 47 Belgrave Square, London SW1X 8QX.