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In this manuscript, the results of our photochemical studies in which water-soluble poly(ether imine) dendrimers are used as reaction media are presented. The selectivity obtained in four independent photoreactions suggests that dendrimers provide a much better constraint than a conventional micelle. The dendritic microenvironment not only restricts the mobility of radical intermediates, but also rigidly encapsulates the substrate, intermediates and products from exiting to the bulk environment. In the context of "Green Chemistry", reactions inside aqueous dendritic media provide opportunities to perform organic reactions in water.