XXIX PANHELLENIC CONFERENCE ON SOLID STATE PHYSICS AND MATERIALS SCIENCE

22-25 September 2013

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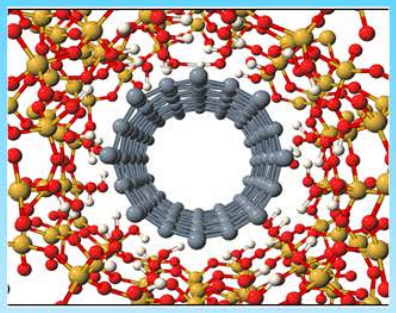
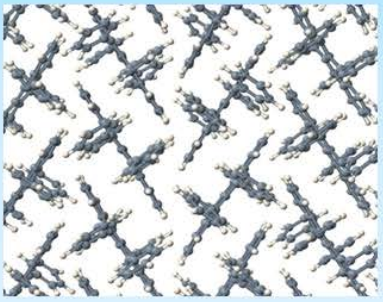
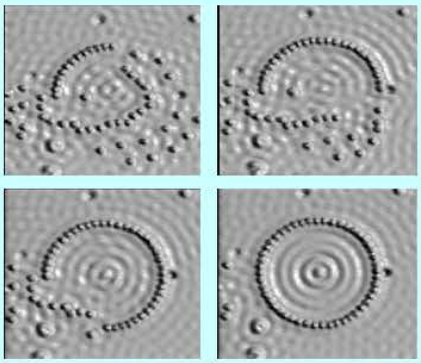


Topics:

- Photonics and Optoelectronics – Electronic and optical properties, semiconductors and devices
- Structural, dynamical, and mechanical properties of condensed matter
- Strongly-correlated systems, magnetism, and superconductivity



- Physics of surfaces, the nanoscale, and low-dimensional systems
- Polymers, organic materials, biomaterials
- Ceramics, composites, minerals, metallic and novel materials



Deadline for Submission of Abstracts:
June 15, 2013

Early Registration Deadline:
July 31, 2013

URL: http://physics.ntua.gr/xxix-pcssp/

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Tuesday, September 24, 2013

13:00-15:00 Poster Session P02/Light Lunch

P02.01	**Stuctural and electromagnetic characterization of ferrite magnetodielectric materials for microwave applications**, *E. Varouti*[1], *E. Manios*[1], *D. Stamopoulos*[1], *M. Pissas*[1], *A. Alexandridis*[2], *T. Zervos*[2], [1]Institute for Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, NCSR Demokritos, 15310, Athens, Greece, [2]Institute of Informatics & Telecommunications, NCSR Demokritos, 15310 Athens, Greece
P02.02	**Magnetic Properties and Structure of Fe Doped Mn-Ni-Sn Ribbons**, *C. Sarafidis*[1,2], *M. Gjoka*[2], *O. Kalogirou*[1] *and D. Niarchos*[2], [1]Third Lab. of Physics, Physics Dpt, Aristotle University of Thessaloniki, Greece, [2]Institute for Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems NCSR Demokritos, Agia Paraskevi, Greece
P02.03	**Aging effects in $YBa_2Cu_3O_{6-x}$ single crystal with critical temperatures near the spin glass-superconducting phase boundary ($0<T_c<30$ K)**, *G. Papageorgiou*[1,2] *and M. Pissas*[1], [1]Institute of Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems, NCSR Demokritos, [2]Physics Department, National and Kapodistrian University of Athens
P02.04	**Study of FePt-C/SiO_2 thin films for magnetic recording applications**, *G. Giannopoulos, Th. Speliotis and D. Niarchos*, IAMPPNM , NCSR Demokritos, Athens 15310,Greece
P02.05	**Orbital and spin order transitions in $La_{1-x}Nd_xMnO_{3+\delta}$ ($\delta \geq 0$) perovskite compounds**, *K. Georgalas, E. Syskakis*, Section of Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, Gr-15784 Zografos, Athens
P02.06	**Engineering Hidden Order Parameters And Quartets In Correlated Nanostructures**, *G. Livanas*[1], *G. Varelogiannis*[1] *and P. Christodoulou*[1], [1]Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece
P02.07	**Angular dependence of the peak effect in $MgB_{2-x}C_x$.**, *I. Amvrazi*[1,2] *and M. Pissas*[1], [1]Institute of Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems, NCSR Demokritos, [2]Physics Department, National and Kapodistrian University of Athens
P02.08	**Magnetism in binary and encapsulated Co-O clusters**, *D. Tzeli*[1], *A. Morphis*[1], *J. A. Blackman*[2], *and K. N. Trohidou*, [1]IAMPPNM, Department of Materials Science, NCSR Demokritos, Athens, Greece, [2]Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, United Kingdom
P02.09	**Perpendicular magnetic anisotropy in W—CoFeB—MgO magnetic heterostructures**, *Th. Speliotis, V. Psycharis, A. Kaidatzis and D. Niarchos*, Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, National Center for Scientific Research Demokritos, 15310 Athens, Greece, , *tspeliotis@ims.demokritos.gr
P02.10	**Theoretical and experimental study on the stray magnetic field produced from cracks on ferromagnetic material**, *I. Kaliakatsou-Papakosta,*[1,2] *E. Manios*[1], *and M. Pissas*[1], [1]Institute for Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems, NCSR Demokritos, [2]Department of Physics, National and Kapodistrian University of Athens
P02.11	**Suppression of the Jahn Teller distortion in $LaMn_{1-x}Fe_xO_{3+\delta}$ ($\delta \approx 0$) compounds**, *G. Vertsioti, M. Calamiotou, E. Syskakis*, Section of Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, Gr-15784 Zografos, Athens
P02.12	**Confined 1,4 cis Polyisoprenes within Self-Ordered Anodic Aluminum Oxide Effect on the Segmental and Global Dynamics**, *S. Alexandris*[1], *M. Steinhart*[2], *G. Floudas*[1], [1]Department of Physics, University of Ioannina, [2]Institut für Chemie neuer Materialien, Universität Osnabrück
P02.13	**β-Cyclodextrin Molecularly Imprinted Polymers (β-CyD MIPs) for dye binding**, *G. Z. Kyzas, N. K. Lazaridis and D. N. Bikiaris*, Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece
P02.14	**HA Coatings Reinforced by La_2O_3, Sm Doped CeO_2 and Cu-Zr-Al-Ag Metallic Glass Addition on Metal Substrate: Bioactive Behavior Evaluation**, *G. Theodorou*[1], *M. Perissi*[1], *L. Papadopoulou*[2], *N. Kantiranis*[2], *S. Yugeswaran*[3], *A. Kobayashi*[3], *K. M. Paraskevopoulos*[1], [1]Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece, [2]School of Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece, [3]Joining & Welding Research Institute, Osaka University, Osaka 567-0047, Japan
P02.15	**Thermoresponsive Aggregation of PS-PNIPAM-PS triblock copolymer in aqueous solutions**, *A. Papagiannopoulos*[1], *J. Zhao*[1], *S. Pispas*[1] *and A. Radulescu*[2], [1]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece, [2]Institute for Solid State Research, Research Centre Jülich, 52425 Jülich, Germany

β-Cyclodextrin Molecularly Imprinted Polymers (β-CyD MIPs) for dye binding

G. Z. Kyzas*, N. K. Lazaridis and D. N. Bikiaris

Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece

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Molecular imprinting is a method of inducing molecular recognition properties in synthetic polymers in response to the presence of template species during formation of the 3D structure of a polymer. The history of molecular imprinting is traced back in 1940s and 1950s, that roused the inspiration to create affinity for dye molecules in silica gel (based on theory of Linus Pauling), which is considered to be the first imprinted material [1]. Since then, many research groups worldwide have studied the synthesis of highly specific molecularly imprinted polymers (MIPs) [2]. The main field of imprinting includes separation processes (chromatography, solid-phase extraction, membrane separations), artificial antibodies, and sensors recognition elements [3]. MIPs present wide recognition due to their stability, ease of preparation, and low-cost potential [2]. The imprinting technique involves the formation of a pre-polymerization complex between the imprinted molecule (usually has relatively low molecular weight) [2], and the functional polymer with specific chemical structures designed to interact with the former either covalently or non-covalently (basic interactions). Based on the above consideration, the selection of a suitable polymer and optimization of appropriate polymerization conditions (cross-linkers, initiators, polymers) are crucial for the improvement of MIPs performance.

In the current study, β-cyclodextrin reagent was selected as the crucial substrate of MIPs synthesis, given the published data revealing the advantageous characteristics of those reagents [4]. Cyclodextrins (CD), characterized as supramolecular host compounds, belong to a series of cyclic oligosaccharides. In particular, β-CD is formed by the binding of seven individual d-(+)-glucopyranose units through α-1,4-glycosidic oxygen bridges. The physical conformation of its molecular structure creates a lipophilic inner cavity with hydrophilic outer surfaces that is able to interact with a large variety of guest molecules forming non-covalent inclusion complexes. Compared with the functional polymers of conventional MIPs, β-CD, as a new generation of functional polymer, possesses some unique advantages. Firstly, β-CD host-guest inclusion complex and β-CD polymer orderly assembly are easily formed under mild conditions. Secondly, due to the rigidity and chirality of hydrophobic cavity, β-CD unit can form complex with the target molecule through various intermolecular interactions (van der Waals forces, electrostatic affinity, hydrophobic, dipole-dipole, and hydrogen bond interactions) during the imprinting process. This is helpful for obtaining high affinity binding sites. Moreover, owing to the rapid and reversible interaction between β-CD and guest, the prepared MIPs can be easily regenerated by suitable regulation and control. Therefore, by introducing β-CD supramolecular chemistry into molecular imprinting technique, both the preparation process of MIPs, and the recycle of the artificial receptors is more direct and simple. Furthermore, β-CD-based imprinted polymers are thought to be advantageous compared to previously employed methods of producing MIPs [5]. The latter is due to the ease of condensation polymerization process, using simple neutral molecules such as epichlorohydrin or toluene diisocyanate. The polymerization process can be carried out under standard laboratory environment (25 oC, 1 atm), without the need of drastic conditions. In this case, β-CD itself can serve both as polymer to interact with template molecules, and as cross-linker to form a 3D polymer matrix. It is worthy to note that this system does not need any initiator or catalyst of cross-linker. The latter simplifies the whole polymerization process, avoids interfering effects caused by these molecules (such as creation of non-specific binding sites), and hinders the leaching of template during template removal process.

Although the molecular imprinting technique has been widely used for polymer synthesis with various drugs and proteins as template molecules, the behaviour of MIPs in environmental targets (e.g. industrial wastewaters) has been hardly examined [4]. It is notable that a limited number of works deals with the recognition of dye molecules as templates [6-8]. The novelty of the current study is: (i) the environmental target as template molecule used (dye), as well as the optimized conditions (ii) in polymerization/imprinting stage, and (iii) in rebinding/adsorption step employed. Consequently, variable parameters of polymerization (polymer, cross-linker, and initiator) were examined to assess the effect of "polymer cookery" in selectivity and adsorption capacity of the prepared β-cyclodextrin MIPs.

[1] Dickey F. H., J. Phys. Chem. 59, 695 (1955).
[2] Liu J. –Q., Wulff G., J. Am. Chem. Soc. 124, 7452 (2004).
[3] Chen L., Xu S., Li J., Chem. Soc. Rev. 40, 2922 (2011).
[4] Yu Q., Deng S., Yu G., Water Res. 42, 3089 (2008).
[5] Hishiya T., Shibata M., Kakazu M., Asanuma H., Komiyama M., Macromolecules 32, 2265 (1999).

β-Cyclodextrin Molecularly Imprinted Polymers (β-CyD MIPs) for dye binding

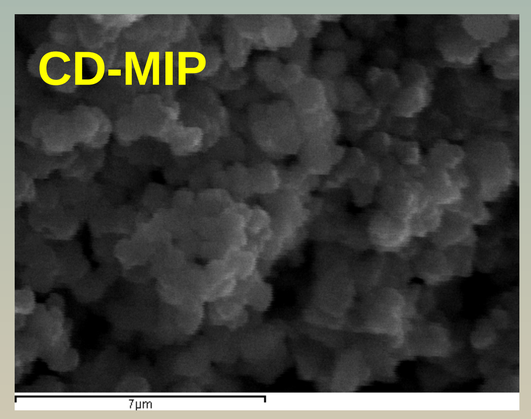
George Z. Kyzas, Nikolaos K. Lazaridis, Dimitrios N. Bikiaris

Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece

Synthesis

Most of the imprinted polymers were prepared by the following "one-step method". This method takes advantage of in situ formation of the β-CD-dye complex in the polymerization mixture. β-CD (5 mmol) and dye template (RO, 600 mg) were dissolved in 50 of dimethylsulfoxide (DMSO), and then 25 mmol of TDI were added. After being magnetically stirred at 65 °C for 2 h, the gel formed was chopped into pieces, washed with acetone, and ground with mortar and pestle. The polymer was sufficiently washed with hot deionized water, and hot ethanol for the removal of the residual quantities of dye templates, β-CD, and TDI. Then, the polymer was dried in vacuum at 40 °C for 24 h. As a control, blank microspheres were prepared with the same procedure in the absence of the template molecules; these polymers obtained were the non-imprinted polymers (CD-NIPs).

SEM



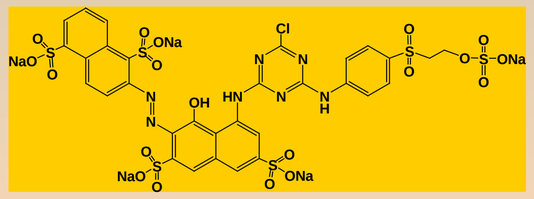
Adsorption procedure

The influence of pH on dye adsorption was studied by mixing 0.05 g of MIPs with 50 mL of an aqueous dye solution (C_0=50 mg/L). Immediately after mixing, the suspension was allowed to rebind/adsorb dyes by shaking for 24 h (contact time). The temperature was maintained constant at 25 °C using thermostatically controlled water bath (Julabo SW-21C). The pH value, ranging between 2 and 12, was kept constant throughout the whole adsorption process with micro-additions of 0.1 M HNO_3 or 0.1 M NaOH. Similarly, the effect of pH on desorption of the adsorbed dye from MIPs was studied in a batch experimental set-up. After adsorption (at the optimum pH found), the samples were collected and filtered using 0.45 μm pore-sized membranes. A small fraction of the dye (~1-2 %) and the adsorbent (~1%) were retained on the filter membrane; these small variations due to filtration were neglected. Desorption experiments were performed by mixing the collected amount of dye-loaded MIPs with aqueous solutions over a pH range of 2-12. After 24 h of shaking at 25 °C, the samples were collected and analysed for determination of the optimum desorption pH.

Batch kinetic experiments were performed by mixing a fixed amount of MIPs (0.05 g) with 50 mL of an aqueous dye solution (50 mg/L). The suspensions were shaken for 24 h at pH=2 (optimum adsorption pH value found from the pH-effect experiments) in water bath at 25 °C. Samples were collected at fixed intervals (5 min - 24 h) and analyzed using a UV-Vis spectrophotometer.

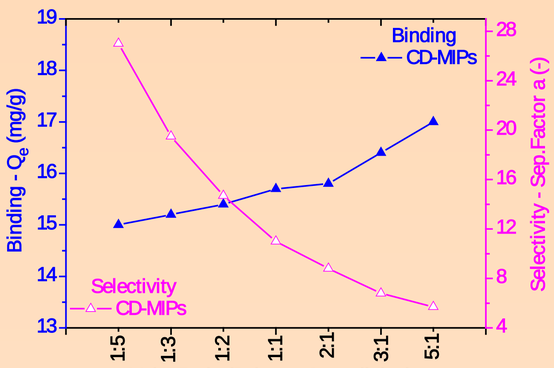
The effect of initial dye concentration was determined by contacting 0.05 g of MIPs with 50 mL of aqueous dye solutions (C_0=10-70 mg/L). Immediately after mixing, the suspension was allowed to rebind dyes by shaking for 24 h (at pH=2, determined as optimum value) at 25 °C. The same experiments were repeated at 45, and 65 °C. Same experiments were performed for the respective NIPs.

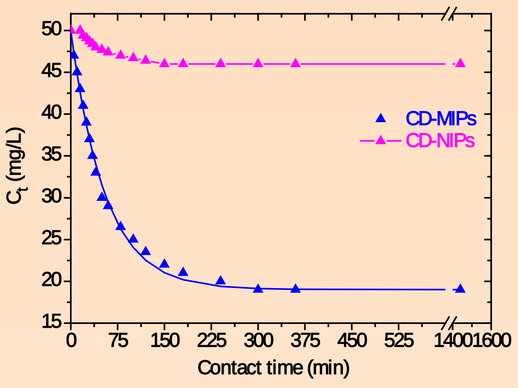
Dye template

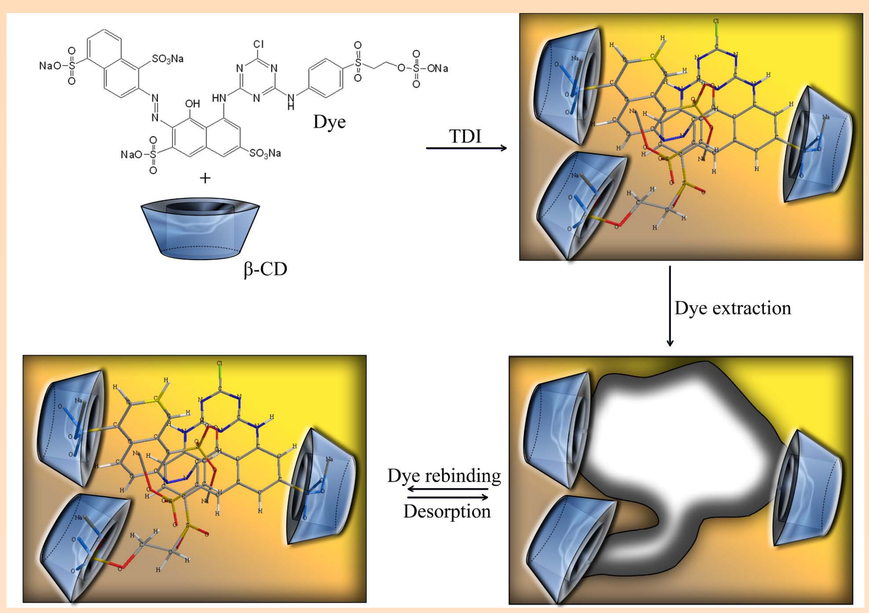


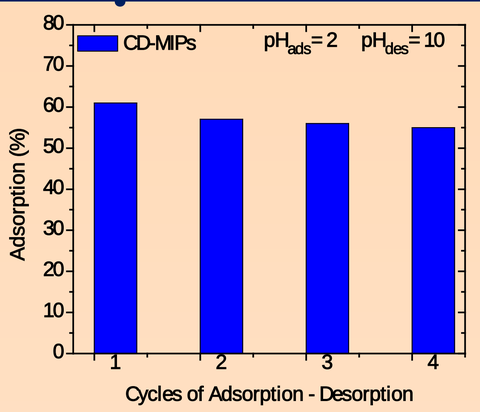
CI Reactive Orange 16 (Brilliant Orange KN-R)

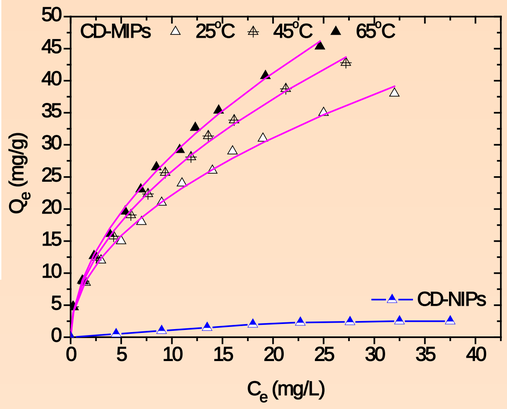
Adsorption - Rebinding experiments

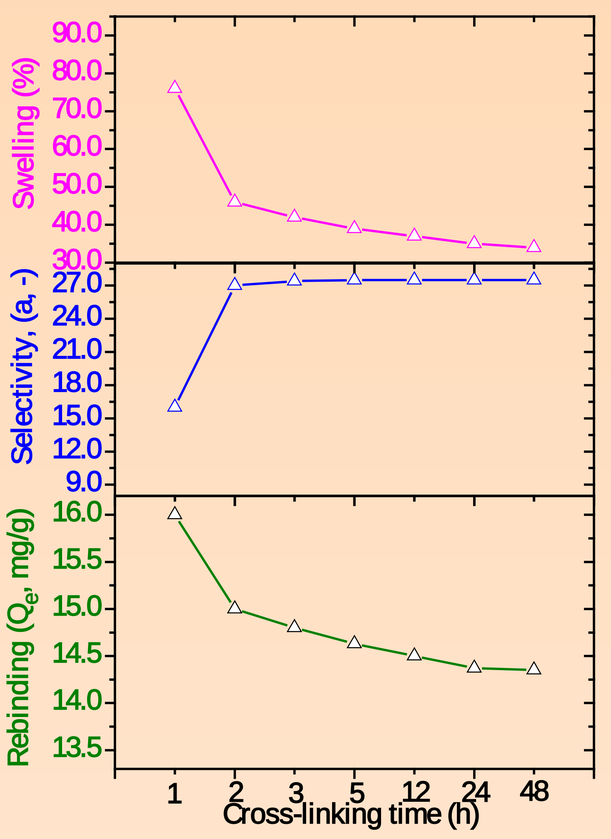












Selectivity

The next Table shows the experimental results from the rebinding experiments in thrichromatic dye solutions. The dye-MIPs prepared rebind with selectivity to the OR molecule (template) from a trichromatic dye solution in the presence of other reactive dyes, presenting high distribution coefficients. The simultaneous adsorption of small amounts of the other competitive dyes (although several dyes had smaller size than the target molecules) could be attributed to the electrostatic attractions developed between MIPs and dye molecules with a non-specific manner. The calculation of the relative separation factors (β) of CD-MIPs showed that the imprinted matrix was specific and approximately 20 times greater than the non-imprinted ones (CD-NIPs). Therefore, the selectivity of MIPs against their respective NIPs is doubtless and definite.

Table. Effect of imprinting on selectivity of CD-MIPs and CHI-MIPs.

	CD-MIPs		CD-NIPs		
Dye mixture	K_D (L/g)	α	K_D (L/g)	α	β
RO	3.000	-	0.111	-	-
RY	0.212	14.15	0.087	1.28	11.09
RB	0.176	17.05	0.099	1.12	15.20

Adsorption conditions: C_0=20 mg/L for each dye; pH=2; T=25 °C; t=24 h.

Conclusions

Increasing the percentage of polymer versus cross-linker the selectivity of MIPs was decreased, while a slight improvement in dye rebinding was observed. Increasing the polymerization time, the selectivity of MIPs was improved, while a slight diminishment in dye rebinding was observed. Higher dye rebinding was achieved at pH=2 and higher desorption percentages at pH=12. Pseudo-first order model presented the best theoretical correlation and the equilibrium was reached within 4 h. The MIPs prepared showed capacity up to 35 mg/g. The loss in the dye rebinding between the first cycle of regeneration and the last one was negligible, therefore the materials can be easily used repeatedly. The dye-MIPs prepared presented high selectivity to the OR molecule (template) from a trichromatic dye solution in the presence of other related dyes.

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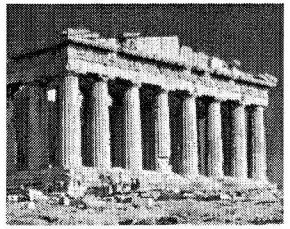

CERTIFICATE OF ATTENDANCE

This is to certify that

Dr. George Z. Kyzas

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